Ministry for the Environment
Manatū Mō Te Taiao

The Effects of Air Pollution on New Zealand Ecosystems

Review of National and International Research

Prepared by Environmental Science & Research Limited in collaboration with the University of Waikato, Hort Research, the University of Queensland and Pacific Air and Environment

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1. EXECUTIVE SUMMARY

This review represents an assessment of information currently available in the literature covering the potential affects of ambient air pollution on ecosystems, where "ecosystem" is defined as excluding human health only. The information gathered is then used to assess potential effects in the New Zealand situation, by identifying the pollutants most likely to cause adverse effects in New Zealand. The information gathered is to be used in reviewing changes to the New Zealand Ministry for the Environments' Ambient Air Quality Guidelines.

The pollutants discussed include oxides of nitrogen, sulphur dioxide, ozone, particulates and fluoride. The effects reviewed include those on plants, birds and insects.

Plants are identified as the organisms with most potential to receive impacts from ambient air pollution. When the findings are compared with current MfE guideline levels, the existing ozone and sulphur dioxide guidelines are found to be in need of change to take into account the potential affects on plants. It is also recommended that the existing nitrogen guideline be expanded to include the potential for all ambient nitrogen to impact on plants and ecosystems.

2. INTRODUCTION

The New Zealand Ministry for the Environment has commissioned ESR and collaborators from the University of Waikato, Hort Research, University of Queensland, Pacific Air and Environment and the Queensland Department for the Environment to undertake a review of the potential impact of ambient air pollution on New Zealand Ecosystems.

The purpose of this review is to focus on the analysis of relevant information, and form an understanding of important elements of ecosystem stress from air pollution, and how it applies to the New Zealand situation. The work will further focus on how this can be included by the New Zealand Ministry for the Environment's review of ambient air quality guidelines, and will focus on;

- identifying those air pollutants most likely to cause adverse effects on New Zealand ecosystems, and the major sources of those pollutants
- identifying those New Zealand plant and animal species that may be sensitive to air pollutants and poor air quality, and how impacts upon individual species may provide guidance to impacts on the wider system
- recommend ambient air quality guidelines for the pollutants identified to protect New Zealand ecosystems, based primarily on overseas information
- identify appropriate ways to investigate the effects on New Zealand ecosystems and whether overseas guidelines can be applied to New Zealand.

2.1 Acid Rain and Acid Deposition Mechanisms and Meteorological Influences

Acid gases such as SO_2 and NO_x are emitted from both natural and anthropogenic sources. They are transformed in the atmosphere to sulphuric and nitric acids, which can be further transformed into aerosols. The acids, the gases and their aerosol products are returned to the earth's surface via two main mechanisms:

- wet deposition in rain or snow (known as acid rain);
- dry deposition, in which particles and gases are deposited directly on water, soil, vegetation or other surfaces.

The natural sources of acid gases contribute to the global nutrient cycle. Acid deposition is often taken to refer to situations where the anthropogenic contribution overwhelms the natural component. In New Zealand, the substantial level of volcanic activity, the relatively low level of fossil fuel combustion (especially for power generation) and the relatively small distances to open seawaters would suggest that the potential for acid deposition is generally limited compared to other industrialised countries. However, localised effects may occur.

Acids and their precursors typically have atmospheric residence times of a few days, and tend to be deposited within a distance of several hundred kilometres of the source.

The transport of acids, gases and aerosols depends on the three-dimensional flow characteristics of the lower atmosphere, which can be highly complex in regions of coastal and mountain terrain, both of which are common in New Zealand. Trajectories of plumes are influenced not only by the prevailing winds, but also by blocking and diversion effects near hills and mountains, slope flows, seabreezes, landbreezes and other effects. In such situations, plume material can be very widely and unevenly dispersed.

Studies in Australia have indicated that for very large SO_2 sources, dry deposition levels are elevated above background to about 40 km. The dry deposition process is strongly influenced by the role played by atmospheric turbulence in mixing the plume to ground level. The rate of deposition is a function of many individual factors, only some of which include plume concentration, aerodynamic roughness, atmospheric stability, friction velocity, temperature, humidity and stomatal resistance.

Often included in the definition of dry deposition is cloud water deposition. Acid aerosol can be absorbed into cloud water, and deposition occurs when clouds impact on terrain. Vegetation often acts as an efficient collector of cloud water. In New Zealand, with a dominance of humid cloudy climates and complex terrain, the potential exists for this mechanism to be locally significant in relation to acid deposition if the source and receptor relationships are satisfied.

Wet deposition is an efficient process for removing water-soluble gases, aerosols and particles from the atmosphere. It proceeds through two possible pathways: washout and scavenging. Washout refers to the process by which the gas or aerosol is absorbed by cloud droplets and eventually falls to the surface in precipitation. In the scavenging process, the precipitation absorbs the gas or particle after it has commenced its descent from the cloud.

The processes involved in wet deposition, especially in the form of washout, are particularly complex, especially with regard to analysis and prediction, since they involve the formation of rainfall in addition to the transport of a polluted air mass. The trajectory is more complicated in a cloudy environment since the release of latent heat generates or enhances vertical motions that are critically dependent on local initial conditions, and critically important in determining where the air mass will travel. Thus, washout can occur over a wide range of distances and directions from the source.

Studies in Australia, which like New Zealand has negligible trans-boundary transport of anthropogenic air pollutants from other regions and relatively discrete source areas of anthropogenic acid gas emissions, have been limited in being able to determine the relative importance and environmental impacts of wet and dry acid deposition. Clearly, however, areas with higher frequencies and durations of rainfall are more likely to have a higher proportion of wet deposition.

Any national assessment of the impact of acid deposition must involve quantitative determination of both total deposition (wet acid deposition plus dry acid deposition) and the critical loads for affected areas.

2.2 Plants

Adverse air pollution effects on plants have long been recognised and the main contributory factors (especially ozone, $S0_2$, $N0_2$) are well known. Usually, however, this relates to visible external injury, even plant death, and direct effects on growth and photosynthesis. Less obvious and therefore less well studied are the more indirect effects of air pollution on flowering, pollination and seed set. These factors are perhaps not of immediate importance to the short-term survival of the individual plant, but of critical importance to the long-term survival of that plant species, any economic or commercial benefits that may accrue, and to the well-being of the affected ecosystem, at large.

There is very little direct information on the effects of air pollution on New Zealand ecosystems, or on plant species occurring naturally in the country. However, because of the importance of introduced plants to the economy of New Zealand, there is much more information that may be applied to the topic, although the conditions under which most of the information was gathered may not be directly relevant to New Zealand. Even the applicability of overseas information cannot be tested rigorously, because the seasonal conditions used in the studies may be quite different from those in New Zealand.

In contrast, there has been a large investment of resources into research on air pollution effects, particularly in north America, and particularly in relation to acidic precipitation and oxidants. Even the earlier attention to the direct effects of sulphur dioxide has been eclipsed, and essentially local air pollutants such as fluoride are rarely examined at present. Consequently, this review will concentrate on effects of oxidants, as many of the physiological consequences of sulphur dioxide result from the oxidative properties of this gas.

An important feature of recent research has been the integration of studies over different scales of organization, with emphases on metabolic effects (Koziol and Whatley 1984, Alscher and Wellburn 1994, Percy *et al.* 1994), agronomic aspects (Unsworth and Ormrod, 1982, Heck, Taylor and Tingey 1988), ecological and genetic (Ulrich and Pankrath 1983, Legge and Krupa 1986, Scholz, Gregorius and Rudin 1989, Smith 1990, Taylor Pitelka and Clegg 1991), although comprehensive assessments continue to be made for a wide variety of pollutants and plant conditions (Yunus and Iqbal 1996), or for particular vegetation types (Olson, Binkley and Bohm 1995) or pollutants (National Research Council 1971, 1977a,b, 1978, Lefohn 1992). It is not intended to compress this information into a few pages, but to highlight some physiological evidence that may guide consideration of air pollution effects on vegetation in New Zealand.

2.3 Animals

The effects that dry deposition air pollution can have on animals ranges from extreme cases where death results, to, more commonly, reduced growth and development, and impaired reproduction ability. Some studies have determined that high levels of various substances accumulated by animals as a result to air pollution exposures can be used as indicators of pollution. Wet deposition, with the exception of spray drift exposures, tends to have a more indirect affect on animals. Where significant changes to ecological chemistry has resulted, there is often a major flow-on effect throughout the system and food chain, resulting in imbalances which lead to nutritional problems or starvation of animals.

There have been some attempts to investigate the direct and indirect affects air pollution may have on bird populations. Passerine (perching) birds have larger numbers of erythrocytes and higher concentrations of haemoglobin, compared to other birds and mammals. This is thought to be a physiological adaptation to the high metabolic requirements of flight. Llacuna et al (1996) established that some Passerine birds living in the Cercs area, Spain, in the vicinity of a coal fired power station, displayed haemotological changes similar to those found in studies on small mammals after inhaling high levels of SO_2 Passerine birds living in polluted and non-polluted zones - even where acid precipitation did not necessarily result in the acidification of water bodies - in Northeast Spain displayed levels of Cr, Al which were higher for birds living in polluted zones (Llacuna 1995); and that the degree of uptake of specific metals was species specific. Birds which ate only vegetation had lower levels than birds which ate other animals.

Pigeons living in Amsterdam have been assessed as bioindicators of air pollution, using isotope identification of lead sources (Schilderman et al, 1997). Similarly, cattle egrets and laughing gulls inhabiting the Galveston Bay region of Texas showed increased lead, cadmium and manganese, although much of the exposure is dietary, these birds were also suggested bioindicators of these toxic substances (Hulse et al, 1980).

Fledgling birds have also suffered as a result of spray application. Birds time the rearing of offspring to coincide with ultimate food availability. Unfortunately, for birds which eat insects, this timing also coincides with crop maturity and insect population explosions. Crops which were sprayed with insecticide had serious consequences for fledglings (Cordi et al, 1997), resulting in death for the smaller chicks, who did not have enough body mass to cope with the toxicity.

Butterflies have also been shown to be adversely affected by spray drift (Dover et al 1990; Davis et al 1991; Cilgi and Jepson, 1995).

The examination of albumin protein adducts in woodchucks (Quebec, Canada) has been suggested as a bioindicator of contamination by PAHs (Blondin and Viau, 1992).

2.4 Synergistic and Additive Effects

Typically, air pollution from any one source exists as a mixture of gases and particulates, interacting with each other and other natural emissions, and undergoing complex chemical changes. Many studies have focused on the direct effects on a species, for expediency in understanding singular effects, of only one pollutant. Reaching an understanding of the direct consequences of a mixture of pollutants is far more difficult. The synergistic and additive effects of mixtures will be examined as part of the effects on species as appropriate.

However, there are many examples of synergistic effects on ecosystems. These particularly include the acidification effects resulting from largely wet deposition of acid pollutants in vulnerable systems. Examples are the acidification of lakes, and subsequent alteration to the food chain, in North America, and the acidification of soils overlying granite and gneiss parent rock in northern Europe. These examples are well documented and understood, and valuable in identifying vulnerable ecosystems and dangerous pollution scenarios.

Individual pollutants may also interact. Accumulation of fine particle acid aerosols in the atmosphere can increase the residence times of 0_3 and the potential for adverse environmental effects. However, there are few studies, if any, on the effects of fine particle aerosols on vegetation (Herzfeld 1982; Gmur et al 1983). The presence of $S0_2$ may also actually increase the sensitivity of plants to ozone injury (WHO, 1987). Another complicating factor is that plant species may vary in their sensitivity to air pollutants at different stages in their life cycle. (Most tree species, for example, are considered to be most sensitive to acute 0_3 exposure during the 8-13 week period after the onset of spring growth . This has been shown for both 0_3 and $S0_2$ (Krupa et al 1989; Luxmoore 1988) but is a poorly understood area of research, as crop phenology is rarely considered. Most empirical models do not consider this aspect, as they deal with only single points. “Phenomenological models”, in which “the occurrence of pollutant episodes must coincide with sufficient frequency with the sensitive growth stages of the plant to result in adverse effects on plant growth and productivity” have yet to be fully developed (Luxmoore 1988). Some mathematical models, aimed at integrating pollution and plant growth parameters to predict cause-effect relationships, are available (Krupa and Nosal 1989; Krupa and Nosal 1989) but need to be improved further.

2.5 The New Zealand Situation

It is the aim of this work to review the current state of international knowledge and how this may relate to New Zealand, and to identify major and significant sources of air pollution, and impacts they may have on flora and fauna in New Zealand; and to identify current gaps in knowledge, and highlight areas for future investigation.

As with the overseas situation, the air pollutants with the greatest potential to impact New Zealand ecosystems are sulphur dioxide, nitrogen dioxide, ozone, fluoride and particulate species. Because the emissions to air of NOx and SO_2 are substantially lower in New Zealand than they are in other parts of the world where adverse effects have been studied, the impact of these pollutants will be largely local. This is even more so for fluoride, and the heavy metal component of particulate deposition. Ozone is the only pollutant which has the potential for a “regional” effect, in that it is capable of causing damage at a considerable distance from the source of its precursors.

2.5.1 Acid Rain

The key processes involved in acid rain formation are the oxidation of the primary pollutants SO_2 and oxides of nitrogen to sulphuric and nitric acid respectively. Although substantial amounts of sulphur dioxide are involved in dry deposition processes of which plant uptake will usually be the major contributor, this uptake does not result in acid generation provided the sulphur dioxide is used as a nutrient. Accordingly most dry deposition of sulphur dioxide does not contribute to soil acidification.

Rates of oxidation of sulphur dioxide and NOx to their respective acids are of the order of 1% per hour. They tend to be higher during the day and low at night. Typical average wind speeds in NZ are about 5m/s. Most of the country is less than 200km wide, and the prevailing wind directions are across the country. This means that typically only about 10% of emitted sulphur dioxide and NOx will have been oxidised before being blown off-shore. This situation is markedly different from the European and North American continents, where distances of thousands of kilometres can be involved, and correspondingly much higher oxidation percentages occur. This means that the concentrations of acid in NH atmospheres would be substantially higher than those in NZ, even if emission rates of SO2 and NOx were no higher than here.

The other factor required is either rainfall or cloud or mist which can scavenge or wash out the acids in the atmosphere. Since these only occur for a fraction of the time only a very small percentage of the sulphuric acid and nitric acid formed will be deposited in NZ.

2.5.2 Plants

An important additional factor to be considered in the new Zealand situation is the very different climatic regime from those of the Northern Hemisphere studies. Most forest decline attributed to air pollution influences, for example, has occurred in primarily boreal forest types at high altitudes. The highest pollutant concentrations occur during colder winter months, and these are conditions which give rise to physiological responses by plants which increase the potential for uptake of gaseous pollutants during normal plant gas exchange processes - increased stomatal conductance, high relative humidity and soil moisture deficit. In the boreal forests, where acid precipitation is high, it becomes become concentrated in snow fall, and is released as an acid pulse upon snow melt.

Dodd and Doley, 1988, demonstrated that one crop species, *Cucumus sativus* (cucumber) shown to have high SO_2 sensitivity when grown under an environmental regime which produced short photoperiods, low temperatures and light intensities (conditions which depress growth rate and increase sensitivity to SO_2), showed reduced sensitivity when grown under tropical environmental conditions of high light intensities and temperatures.

3. MULTIDISCIPLINARY ECOSYSTEM STRESS AND AIR POLLUTION

There are numerous documentaries of studies carried out on the effects of certain pollutants on determined flora and fauna. These have provided a wealth of information on the physiological processes and reactions triggered when the organism is exposed to a certain pollutant. In fact, species are rarely exposed to a single pollutant - the norm is for exposures to mixtures of pollutants the composition of which is primarily determined by the source, and secondarily by the meteorological conditions at the time. It is much more difficult to evaluate the additive and synergistic effects of pollutant mixtures, and even more difficult to determine the overall effect of such exposures on whole ecosystems. Nevertheless, much progress has been made from these studies in identifying areas for concern and ongoing research.

Plants are an integral basis for all ecosystems, and also most likely to be affected by airborne pollution. Plant uptake of toxic elements, or decline from stress factors, have repercussions all along the food chain. Plants can also affect soil or other growing media conditions as a result of chemical balancing required as a result of exposure to air pollution.

The most common exposures come from NOx, SO_2, ozone, particulate and fluoride. Carbon monoxide has not been considered a threat to flora, and there are no reports of CO levels adversely affecting fauna.

3.1 Nitrogen

Potential ambient air nitrogen oxide pollutants include nitric oxide (NO), nitrogen dioxide (NO_2) the combination of the two commonly referred to as NOx, and nitrous oxide (N_2O). Ammonia, NH_3 also poses a potential pollution problem. The predominant source of NOx pollution is the wide range of combustion processes required to support modern civilisation. While it is not a huge concern in ambient (troposphere) air, nitrous oxide is implicated in climate change reactions in the stratosphere. It is most commonly produced in the denitrification process with increased production resulting from the use of agricultural fertilisers. Ammonia is also produced in recycling processes, from the mineralisation of organic matter, although half the ambient concentration is formed during combustion or the production of agricultural fertilisers. Ammonia has been implicated more recently in forest decline in the Northern Hemisphere.

Compared to other air pollutants, there has been little work done on understanding the ecosystem effects of nitrogen pollution. The greatest potential impact is on vegetation. Since nitrogen is an essential nutrient for plants, the consequences of nitrogen fumigation may not necessarily be negative. The understanding of these effects requires a lot of detailed examination of physiological processes, which to date, has focused mostly on the role of NOx in acid precipitation and forest decline in the Northern Hemisphere. Ammonia has also been implicated as an additional component in forest decline, mostly as a result of the contribution of the ionic product in solution (ammonuim) to wet deposition which accounts for the bulk of reduced nitrogen returning to ecosystems (WHO, 1987).

Total deposition of nitrogen based pollutants is the sum of both dry and wet deposition; and the processes involved are strongly influenced by climatic conditions, as well as the physical properties of the receiving surfaces. Calculations of deposition velocities must consider, in addition to the concentration of the pollutant, ambient wind speed, the leaf aerodynamic resistance (boundary layer) which varies with leaf shape size and orientation. Also, the boundary layer is thinner at the leaf edges, which may explain the increase pollution effects seen at leaf margins.

The waxy cuticle covering epidermal leaf cells increases resistance to gases. However, nitrogen oxides deposited on cuticles may dissociate in the water film and/or react with cuticular wax components, causing damage (WHO,1987).

3.1.1 Dry Deposition

Climatic conditions and plant adaptation influence the degree of stomatal control required for a plant to balance nutrient uptake and transpiration. In the case of NOx, closure of the stomata will reduce but not prevent pollutant uptake, as significant amounts of nitrogen dioxide penetrate the cuticle. As a general rule, a plant resists the effects of nitrogen dioxide better under conditions of low light, humidity and nitrogen status, when stomata tend to be closed.

The ability of plants to remove nitrogen oxides from the air has been demonstrated, but in order to enter a plant cell, the gaseous pollutant must pass through the extracellular water contained in the cell wall. Therefore, the solubility of the gas becomes an important factor in plant uptake. Nitrogen dioxide is very soluble in aqueous cellular environment where it reacts with water to form nitrous and nitric acid. The rapid uptake of NO_2 by the mesophyll cells depletes the intercellular NO_2. Consequently, NO_2 diffusion through the stomata is faster than the diffusion of SO_2 (Lange et al,1989). Nitric oxide has been found to be more soluble in xylem sap than in distilled water. In a plants, xylem sap is continuous with the extracellular water in a leaf, which suggests nitric oxide has enhanced solubility in plants. Nitrogen oxide uptake in plants is also affected by the ability of the plant to assimilate or transform the products of dissociation (nitrite and nitrate ions), and by mesophyll resistance which tends to increase as the leaf ages. Absorption tends to be highest in areas where light intensity and metabolic rates are highest, e.g. near the top of the plant canopy. Upon entering the leaf, nitrate and nitrite is reduced by the leaf mesophyll.

When measurements of ambient air concentrations of NO_2 and SO_2, where NO_2 was higher than SO_2, were compared with forest canopy uptake, it was found that NO_2 uptake was higher than SO_2 uptake. The cellular capacity for the reductive detoxification of NO_2 is high, and the fluxes of NO_2 are low, and it is apparent that NO_2 poses far less of a threat to cellular survival than SO_2. While the cellular demand for reduced nitrogen is high and ambient NO_2 levels are low, NO_2 acts as a fertiliser. However, increased nitrogen availability (soil and air) has the potential to accentuate nutritional imbalances, particularly if other essential elements such as Mg are in short supply (Lange et al,1989).

Nitrogen oxides can act in different ways depending on the dosage to plants. The ability of plants to absorb NOx, at low levels can often lead to a beneficial supplementary foliar fertiliser effect. But when concentrations are in excess to the plants ability to cope, problems of toxicity and injury develop. Much work has been done in trying to determine “toxicity thresholds”. And the development of dose-response curves, all of which is informative, but on a very individually specific level (WHO, 1987).

Exposure to nitrogen dioxide will result in the formation of nitrite in plant leaves, which during daylight is rapidly transformed to ammonia. Damage to plants from high nitrogen dioxide levels is more likely to occur at night than during the day, because the lack of photosynthesis at night results in insufficient adenosine triphosphate and $NADPH_2$, or energy, to carry out the transformations (WHO, 1987).

3.1.2 Wet Deposition

It has been calculated that nitrogen pollution causes 30% of acid wet deposition in Europe, which is accentuated at the time of snow melt, in areas of heavy snowfall. Since snow melt also coincides with a vulnerable development stage for plants, this effect can be irreversible. In poorly buffered soils and wetland systems, when a lowering of pH occurs, increased leaching of nutrients and release of metallic ions such as Al follow, resulting in root injury, reduced growth and increased susceptibility to abiotic and biotic stresses.

When nitrogen is a limiting growth factor, low levels of nitrogen pollution may enhance growth, but increased levels may result in imbalances which lead to disrupted availability.

Eutrophication of oligotrophic ecosystems by nitrogen compounds is a threat. A change in nutrient status will be quickly followed by increased competition from species better adapted to the changed conditions, which may result in the original species being out-competed. Ecosystems most likely to be affected include:

Wetland ecosystems

- Ombotrophic mires (e.g. raised bogs)
- Mires in granite, gneissic regions
- Mires otherwise nitrogen limited

Lakes

- Clear-water lakes with isoetid plant cover
- Lakes with a high number of *Potamogeton* species

Terrestrial ecosystems

- Heathlands with a high proportion of lichen cover
- Low meadow vegetation types on slopes and hills with different substrates characteristics, without added fertiliser and used for grazing or haymaking

- Coniferous forests, especially those at higher altitudes

(WHO, 1987)

3.2 Sulphur Dioxide

3.2.1 Wet Deposition

Wet deposition of sulphur dioxide can affect terrestrial ecosystems either by direct impact above ground, or by indirectly to the soil, thereby producing changes in soil characteristics, such as decreased pH, cation exchange capacity. Forest soils which have granite or porphyry parent rock are particularly vulnerable, as demonstrated in the Black forest in Germany and the Harz Mountains. The 1982 Stockholm Conference on Acidification of the Environment noted that an annual sulphur deposition of 0.5g/m2 per year, equivalent to 5kg/ha presented a potential threat to aquatic ecosystems with limited buffering capacity.

3.2.2 Dry deposition

Sulphur dioxide has the potential to be a more serious threat to plants and ecosystems than NOx. Slovik, (1996), determined in a quantitative analysis of the impact of SO_2 and NOx on Norway Spruce, the relative phytotoxicity of SO_2 to be 2.0 to 2.6 times higher than an equally high NO_2 concentration in air.

Sulphur dioxide uptake by plant leaves is via the stomata, so the greatest potential for damage exists during periods of elevated pollution levels which coincide with times when active gas exchange is occurring in the plant, and stomata are must likely to be open. Stomata are more likely to be closed or restricted during periods of high temperatures and light, or during summer months, and more frequently open during winter months. Unfortunately, this means that plants are most vulnerable at times when pollution levels are also highest. This has had devastating effects on Europe’s boreal forests.

Sulphur dioxide is toxic to plants, having the ability to bleach chlorophyll, and the degree to which a plant can cope is varied. In plants and plant communities, resistance to sulphur dioxide pollution effects varies according to the plant’s stage of development, and other external factors such as soil. These differing degrees of sensitivity can result in changes in interspecies competition, the reduction of sensitive varieties, and the alteration of the structure and function of the community. The secondary succession processes that follow will then impact on the consumers and decomposers in the ecosystem(WHO, 1987).

Part of a plants survival armoury is the ability to detoxify toxic compounds, e.g. SO_2, and an individual plant will have many biochemical and physiological routes available to do this; but in doing so, the plant must also maintain the single most important function in order to survive: it must maintain its internal ionic balance.

Exposure to atmospheric SO_2 leads the plant to neutralise and immobilise it into various compounds which it can sequester. Oxidative detoxification of SO_2 is one way, but this can produce cation deficiencies in the plant, which reduce the ability to take up important elements. Long-term resistance to SO_2 using this pathway requires the pant to mobilise cations in the root system on a proton/cation exchange basis. Therefore, cation availability of the soil becomes an important issue, which often requires some form of fertilisation in order to save the plant (Heber and Huve, 1998).

One important strategy involved in sequestering SO_2 involves reductive detoxification. This has significant benefits to the plant, including avoiding the acidification issues which can result from other routes of sulfate accumulation. Herbaceous plants tend to have a lower carbon/reduced sulphur ratio than woody trees. Maize, for example has a 600:1 carbon to reduced sulphur ratio, and spruce trees, 10,000:1. Therefore, for the same deposition of carbon in biomass, maize can deposit much more SO2 as reduced sulphur, than spruce. Plants with lower carbon/reduced sulphur ratios are expected to be less sensitive to atmospheric SO_2(Heber and Huve, 1998).

Agricultural cereal crops in Europe have shown reduced yields as a consequence of elevated sulphur dioxide concentrations. Perennial ryegrass showed reduced growth after fumigation with sulphur dioxide at 43ug/m3 over 273 days; tobacco and cucumber following fumigation with 55ug/m3 over 28 days. *Picea abies, Pinus sylvestris* and the broadleaf *Betula pubescens* in field observations of long-term exposures between 20 and 40ug/m3 showed elevated foliar sulphur levels, and injury in leaf tissue.

3.3 Ozone

Ozone is an all-pervasive air pollutant and, since early studies in the 1950s (Haagen-Smit and Fox 1956) it has become recognised as the most important regional-scale phytotoxin. In contrast to sulphur dioxide and acid rain which do not cause acute damage but secondary effects by acting through some mineral imbalance there is considerable evidence, especially in California, of direct damage to plants by ozone. Ozone is also unusual in that it is secondarily produced by an interaction between ozone precursors (nitrogen oxides, carbon monoxide and volatile organic compounds) oxygen and bright sunlight. Thus the higher ozone concentrations can occur at some distance from the original pollutant source of the precursors. The majority of the precursors are the products of cars and other vehicles and, since car utilisation is still increasing, it does seem that ozone levels might be expected to rise in the future.

3.3.1 Production of ozone

Until the 1970s it was assumed that stratospheric ozone was the main source of tropospheric (low altitude) ozone. It became clear in the early 1970s that photochemical production of ozone from nitrogen oxides and volatile organic compounds was a major process contributing the majority of tropospheric ozone (Fishman et al 1979).

The initial reaction is the photolysis of NO_2 to produce activated oxygen which then reacts with more oxygen to give ozone. The ozone can then react with NO to produce NO_2 thus consuming the ozone. In the absence of organic molecules these reactions effectively sum to zero and there is no gain in ozone.

However, the photolysis of O_3 can produce further radicals that react with organic molecules to produce further ozone. The reaction can be summarised as:

$$RH + 4O_2 + 2h\nu = R'CHO + H_2O + 2O_3$$

Where RH is an organic compound and $h\nu$ is light. Ozone production efficiency is inversely related to the NOx concentration for most atmospheric conditions. NOx can vary over three orders of magnitude in the lower atmospheric boundary layer and ozone shows a similar variation. Ozone production can be limited by low NO_2 or low organic molecules.

In the Los Angeles region the levels of ozone within the city remain low because of nitric oxide emissions which react with the ozone. However, in the forested hills around the city, there can be considerably higher ozone levels due to the transport of ozone to the area and then magnification due to the interactions with naturally produced organics from trees eg: isoprene. On a typical day the mountain ozone levels can be 50% higher than in the city. Thus there is major potential for damage in forests adjoining large cities.

Photochemical oxidation of organic compounds can also lead to the production of other compounds including peroxyacetyl nitrate (PAN). Although at lower concentrations these substances can be much more toxic and can affect different plants eg: herbaceous plants rather than trees. However, acute damage seems not yet to occur.

It is also important to remember that ozone levels also depend on wind speed, in essence a doubling of the wind speed will halve the ozone concentration.

3.3.2 Mechanisms of damage to plants

Ozone enters the plant leaf through stomatal pores. Once within the leaf it can react with many organic molecules but is preferentially consumed by fast reactions with certain compounds (Lange et al. 1989). In particular the double bonds of lipids in membranes are preferred substrates and most ozone entering the cell is trapped in the plasmalemma and very little reaches the vacuole. Lipid destruction and oxidation of membrane proteins make the plasmalemma the main target of ozone attack. The biomembranes of cell organelles like chloroplasts also contain a high proportion of unsaturated fatty acid residues. However, the intracellular ozone concentration decreases rapidly with distance from the plasmalemma so that the organelles are normally in little danger. When air ozone levels are very high there can be considerable pigment bleaching and damage to thylakoids in the chloroplast. There can also be oxidation of SH-groups which maintain structure in proteins with the consequence of both structural and enzymatic failure.

Considerable levels of antioxidants do exist within the cytosol of cells and there are also repair mechanisms with the result that low levels of ozone, even if persistent, do not cause any damage.

3.3.3 Ozone levels

There is no doubt that ozone levels have been increasing during this century. Data for ozone in the free atmosphere over Pic du Midi, southern France, and various other stations show a mean level rising form around 20 µg m^{-3} in 1890 to around 120 µg m^{-3} in the early 1990s (Marenco et al. 1994). The largest rate of increase has been from 1950 onwards and is clearly linked to the increasing use of motor vehicles. In the past 20 years and annual rate of increase of 2.4% per year has occurred in Europe (Stockwell et al. 1997). In general an increase of 1% (absolute values) has occurred in USA between 1979 and 1988 (EPA 1991). Considerable fluctuations around the mean can occur and peak values around 120 µg m^{-3} are not uncommon.

There is very little data on ambient ozone available for New Zealand but the mean southern hemisphere levels are 30 - 42 µg m^{-3} over the oceans. This is regarded as the historical background (Scheel et al. 1992) and is probably applicable to New Zealand.

3.3.4 Sensitivity levels for plants

Plants show considerable differences in their susceptibility to ozone. One of the more sensitive are clover species (Ashmore 1984). It is suggested that levels of ozone below the thresholds will not damage the plants, the levels are:

200 µg m^{-3} for 1 hour, 65 µg m^{-3} for 24 hours and 60 µg m^{-3} for 100 day season.

Ozone below these levels is unlikely to affect most sensitive plants. Especially sensitive plants do exist, for instance one cultivar of tobacco, Bel-W3 is used as an indicator of ozone and shows leaf damage at 80 µg m^{-3} .

No values are available for New Zealand plants. There remains the slight possibility that they could be more sensitive than northern hemisphere plants.

The standard methodology to study the effects of ozone is to use chambers that can exclude (activated carbon filters) or add ozone (Manning and Krupa 1992). Using these systems it is possible to measure relative yields in the absence of ozone, at normal ambient levels and with fixed additions of ozone above ambient levels. Substantial declines in yield have been found in these studies.

Treatments	Seed Weight	
	kg ha-1	% loss
Filtered air	5331	-
Non-filtered air	3552	33
Non-filtered + 60 µg m-3	2322	56
Non-filtered + 120 µg m-3	1698	68
Non-filtered + 180 µg m-3	1430	73

Data on Vona Winter Wheat from Kohut et al.(1987).

It is suspected that substantial losses in productivity could be due to ozone, also in combination with other pollutants, as a result of chronic damage in the absence of acute symptoms. It should be remembered that plants do have some protective systems against oxidant damage in leaves but that these are a metabolic cost and continual application would decrease overall productivity.

Early work on the response of plants to ozone exposure (Dugger and Ting 1970, Tingey *et al.* 1973, Ting and Mukerji 1971) demonstrated temporal changes in sensitivity that have been associated recently with the rate of leaf expansion (Heath 1994). The causal agents for these changes do not appear to be tissue concentrations of soluble sugars, or the release of ethylene. However, it can be argued that there must be a relatively straightforward connection, and it is only a matter of identifying the critical process.

Speculation concerning this process will undoubtedly fuel more research, which could involve any of the synthetic processes associated with leaf growth. The fact that the species which show ozone injury most sensitively have characteristically very rapid growth may itself provide a clue to the cause of injury. On that basis, species with shoot flushing, as is seen commonly in tropical environments, might be expected to be sensitive to ozone if leaf area increase is the critical overall process. On the other hand, if the rate of chlorophyll synthesis is critical, flushing species that are slow to green may be less sensitive than species such as tobacco, bean and cotton, in which the leaves are green almost from the time of initiation.

Runeckles and Chevone (1992) indicated that the two biological compounds with the highest *in vitro* rate constants for reaction with ozone are the peptide glutathione and cysteine, the amino acid of glutathione. Glutathione reacts with oxygen produced during photosynthesis to regenerate $NADP^+$, and it is normally present in relatively large quantities. They point out that *in vivo* rates may be effectively lower because of the separation of substrates and active sites within a cell, and the indication that leaf intercellular space ozone concentrations are close to zero (Laisk *et al.* 1989). However, there is clear ultrastructural evidence of the penetration of ozone or a derivative to cell organelles, so the sensitivity of some developmental processes to oxidation state is likely to be very high, even though the quantities may be small and difficult to detect in bulk tissue preparations. Recent developments in immunocytochemistry are likely to enable advances in understanding of critical cellular processes, and improved perspectives on the role of ozone.

3.4 Additive and Synergistic Effects

It is very rare for nitrogen pollutant species to exist in isolation. Most often, they are in association with sulphur dioxide and ozone, both of which are phytotoxic. Summarised reviews of plant responses to exposure to these combined pollutants show that the effects are additive, synergistic or antagonistic (WHO, 1987).

Studies on a few plant species have shown again how important climatic conditions are on the overall effect of exposure to mixtures of pollutants. Concentrations which are damaging in winter can be negligible or even beneficial in summer conditions. NOx combined with SO_2 will generally produce an overall reduction in growth, as well as visible foliar injury at concentrations much lower threshold concentrations than either pollutant alone.

Studies on the combined effects of ozone, SO_2 and NO_2 have suggested a threshold for injury as low as 28.5ug/m^3 NO_2 in association with similar levels of SO_2 (40ug/m^3) and ozone (60ug/m^3).

Peak concentrations of $NO_{2,}$ are often associate with elevated SO_2 levels, but low ozone, due to the scavenging of ozone by nitrogen dioxide. Under these conditions, it has been shown (WHO, 1987) that sensitive plants are adequately protected from adverse nitrogen dioxide effects if the four hour average does not exceed 95ug/m^3.

Because NOx and SO_2 taken up via stomata is not accompanied by an “equivalent” stomatal cation flux, reductive or oxidative detoxification will induce an additional cation demand that must be supplied from the soil, and the quantification of this additional cation demand depends on the growth rate of the plant, and their N, S and cation contents, and on the relative participation of oxidative versus reductive detoxification pathways (Slovik, 1996). The additional cation supply must come from the soil. If there is a cation deficiency in the soil, this must be overcome by fertiliser application, or chronic NOx and SO2 pollution can cause mineral deficiency symptoms. This may lead to reduced canopy and root growth rates as the plant diverts available cations to cope with vacuolar sulphate neutralisation demands. Slovac (1996), states that for Norway spruce, SO_2 concentrations of 85µgm^3 will cause massive competition for any available K^+ budget. His work did not see an equivalent effect from the ambient NO_2 levels encountered, because ambient NO_2 levels (16 - 33µgm^3) were below those required to induce an effect. He lists the combination of environmental conditions required to produce canopy thinning which would exceed the natural dynamics of around 20% as:

- high ambient SO_2 concentrations
- short growth periods (forests at higher altitudes are more vulnerable than those at lower altitudes)
- poor K^+ or Mg^{2+} depleted soils
- acid precipitation, which leads to leaching of K^+, Mg^{2+} into groundwater

- the “export” of K^+ or Mg^{2+} out of the system by

    1. harvesting the crop (wood)

    2. stimulated growth of herbaceous plants and microorganisms

    3. increase in protein phytophage insects, deer, etc

Those components of an ecosystems which are less able to cope with K^+ or Mg^{2+} shortages will not compete, and the result may be a change in species composition (ecosystem drift) and reduced biodiversity.

3.5 Heavy Metal Pollution

The major air pollution source of heavy metal contamination is particulate material, mostly originate from combustion sources. There have been few studies performed which elucidate the effects of particulate deposition on plants. Most work investigating the effects of particulate pollution has focused on the effects of individual components of particulate material and in particular, heavy metals, and it is not possible to relate accumulation either in terms of the levels measured or the rate of accumulation, to simple gravimetric mass measurements of particulate material.

The primary exposure route for birds to heavy metals is from food which has been exposed in some way, either directly from fallout, or ingestion, and therefor heavy metal exposures to birds is largely a secondary effect.

Comparisons of three passerine bird species living in polluted and non-polluted zones - even where acid precipitation did not necessarily result in the acidification of water bodies - in Northeast Spain demonstrated that levels of Cr, Al were higher for birds living in polluted zones (Llacuna 1995); and that the degree of uptake of specific metals was species specific. Birds which ate only vegetation had lower levels than birds which ate other animals.

Aluminium levels above 0.1% of the diet can have an adverse effect by disrupting Ca and P metabolism. An increased intake of Al by insects inhabiting acidic lake waters, and which are a major food source for pied flycatchers in Sweden, has been linked to severe eggshell defects in flycatcher populations nesting near the affected lake (Scheuhammer, 1987). Measurements of Al concentrations in these insects revealed levels up to 1230ug/g dry weight.

Studies by Nyholm et at,(1995) comparing populations of Passerines in Poland (=polluted environment) and Sweden (=clean environment) showed that ambient levels influenced the body burden for the metals Pb, Cd, Hg which are non-essential elements for the birds physiological development, The essential elements Zn Cu, Fe were not influenced by ambient concentrations, and probably subjected to homeostatic control mechanisms. The same study examined haemoglobin levels in the two populations, and found that levels were lower in birds from the polluted environments, however, whether the cause of lowered haemoglobin is due to heavy metal contamination or gaseous pollutants is not clear.

Cd has been demonstrated to be accumulated by birds in the liver and kidneys in excess of the concentrations in their food supplies; and the organ associated with Cd toxicity is the kidney while the liver, which accumulates approximately half the body burden and is generally resistant to Cd toxicity; with the testes of males also affected severely by sub-lethal exposures. Birds accumulating Cd levels of 100-200ug per gram dry weight in the kidneys, have displayed symptoms of Cd induced nephrotoxicity, similar to that found in humans an other mammals (Scheuhammer, 1986).

Severe inhibition of reproductive organs following Hg dietary intake. At levels of 2ppm, delayed testicular development as seen in young quail; levels of 125ppm in drinking water resulted in depressed fertility, and concentrations above 125ppm in drinking water depressed growth rates and increased mortality in young chickens (Scheuhammer, 1986).

Transformation of Hg species in aquatic environments can be complex (Scheuhammer, 1986). The most stable form, MeHg, is the most readily absorbed intestinally, and has been subjected to rigorous study. Species sensitivity to Hg contamination varies; for example, feeding 33ppm Hg (as MeHg) for 35 days to pheasants, ducks chickens resulted in 90%, 85% and 7.5% mortality respectively(Gardiner, 1972 in Scheuhammer, 1986). Piscivorous birds living in a Hg contaminated environment are particularly vulnerable, even if the original source of contamination contained no MeHg. As a result of if its ability to cross the blood-brain barrier birds exposed to this pollutant can suffer spinal cord degeneration. The symptoms of Hg poisoning in birds is similar for many species, and is characterised by reduced food intake which leads to loss of body weight, progressive weakness and difficulty flying or walking and standing, and inability to co-ordinate muscle movements. Death is inevitable. Low doses of 2-3ppm over a period of 12 weeks resulted in liver concentrations of around 2ppm Hg in adults. This affected reproduction, and resulted in an increase in shell-less eggs, decreased hatchability, and an increase in unfertilised eggs.

Lead is absorbed primarily by the bones of birds, and if accumulated in soft tissues, it is mostly by the kidneys. Any excess may be sequestered in the nuclei of cells, where it is bound to nuclear inclusion bodies. Absorption appears to be linked to dietary Ca levels. Female birds will accumulate Pb at a greater rate than males, and this may increase 4-5 times in laying females; which may be related to the greater turnover of skeletal Ca ,which is a result of eggshell formation. This is linked to biochemical processes where increased synthesis of a vitamin D responsive Ca-binding protein appears to be linked to increased intestinal absorption of Pb. Young birds are more susceptible to Pb toxicity, displaying symptoms when crop contents Pb concentration was 80-100ppb, while adult birds from the same nest were unaffected. Growth impairment of nestlings has been associated with kidney levels of around 6ppm, and at 15ppm, survival was at risk. Reproduction does not appear to be affected by dietary levels < 100ppb. Starlings reared with highway verges and exposed to dietary PB levels of around 90ppb displayed decreased brain weights. Some species appear to be more susceptible to Pb toxicity; Japanes quail showed reproductive effects from dietary levels as low as 10ppb, whereas chickens requires over 200ppb to produce similar effects (Scheuhammer, 1986).

* Passerine birds are of the order Passeriformes, perching birds, of the size of a sparrow (The Concise Oxford Dictionary)

4. EFFECT OF AIR POLLUTION ON PLANTS

Plants, in particular trees, are significant interceptors of air pollution in most ecosystems. Plants are effective gas exchange systems, with the exchange occurring mostly (in higher plants) via stomata, since the epidermis provides a protective barrier through which very little uptake occurs.

Trees are long-lived sessile organisms. The significance of this is that, in order to survive frequent changes in their environment, they must achieve a balance between sufficient adaptation to the prevailing environmental conditions, and enough genetic potential to be able to adapt to future environmental conditions. This is essential to ensure stability of forest ecosystems. Individuals, as well as the population, need to possess high genetic multiplicity. Many studies have shown that forest trees have a higher degree of genetic variation than other organisms which are either mobile and can escape adverse environmental conditions or are short lived.

4.1 Means of detecting plant physiological responses to air pollution

4.1.1 Why physiology may be used to detect pollutant effects

Plant responses to air pollution, and to any other environmental factor, can be observed at all levels of organization, from enzymatic, through subcellular organelles, cellular, tissue, organ, organism, community, ecosystem and biome (Osmond 1988, Weinstein 1978, Darrall 1989, McLaughlin 1994). The time scales over which assessments at each level can be made vary as much as the spatial scales, so the speed of response to a change in environmental condition can be detected much sooner at the physiological level (which may span the scales of organization from enzyme to organ) than at the ecosystem or biome level, where responses may take years or decades to appear (Osmond 1988, McLaughlin 1994). The study of physiological responses to pollutants may be justified on the grounds that physiological responses are more sensitive to pollutants than is visible injury, and that physiological processes underlie ecological processes. In the first instance, research issues will be examined, and some reference to the applicability of findings to monitoring will be made where appropriate.

(a) Physiological responses are more sensitive than visible injury

It has been concluded (Guderian 1977,Weinstein 1978) that cellular responses to pollutants are more sensitive than responses at the organism level (such as the growth of plants or plant parts), and that the appearance of injury symptoms is less sensitive than growth (also McLaughlin 1985). In this context sensitivity implies speed of response as well as the concentration of pollutant at which the smallest significant response can be detected. This proposition is reasonable, and generally applicable, but the relationships between growth and symptom expression are not constant for all species and all pollutants. Part of the inconsistency of the relationships between pollutant effects at different levels of plant organisation arises from the response of the plant to other forms of stress which may be expressed in ways very similar to those resulting from pollutant injury. This applies as much to physiological responses as to visible injury, which is well-documented, for example, oxidative enzyme activity may be used as an expression of response to stress, but the reaction is so general that it cannot always be associated with a pollutant of interest.

(b) Physiological responses underlie and precede ecological changes

This proposition is reasonable, provided the correct responses are measured. Where there is a direct connection between a pollutant effect at the cellular or subcellular level and a response at a much larger level of organisation, physiological responses can provide both a sensitive and early indication of ecological change. For example, as will be discussed later, pollen viability and floral fertilisation involve single cells, and the time scale of effects may be minutes, but the effects influence the total organism which may have a life span of centuries.

Where the effects of several or many processes at the smaller scale are confounded as the scale of organisation increases, the and applicability of observations at smaller scales of organisation decreases. For this reason, observations on attributes such as some photosynthetic parameters or tissue nutrient relations are not reflected directly in growth responses of plants or crops (McLaughlin *et al.* 1982, Enders *et al.* 1992, Augustin *et al.* 1998). This dilemma confronts not only pollution scientists, but all those who attempt to predict plant community function for any reason on the basis of fine physiological measurements.

4.2 What are the responses

Ultimately, all responses of plants to any environmental stimulus can be described in terms of the genetic constitution of the cells, and the consequent activation or deactivation of enzymes that determine every physiological and morphological response. Where the responses are dominated by single genes, recognition and control of these molecular markers of activity promise much (Birch 1997), but multiple gene effects are more difficult to discern and even more difficult to control.

In addition, whilst in artificial populations the normal methods of experimental analysis can be applied to discriminate between genetic and environmental influences on phenotypic plant response, different techniques are required in natural populations. Gregorius (1989a) proposed mathematical tests for this discrimination, and although they are beyond the scope of this review, it is necessary to indicate that rigorous sampling and detailed observation are required in order to achieve the required discrimination of phenotypes. A similar comment is warranted for studies on physiological attributes of plants.

(a) Cellular functions

The many functions of cells are so closely related that description under different headings may detract from the integrated view that is essential to an understanding of pollutant impacts. However, a total understanding cannot be created immediately, and must be assembled from components that have been examined under conditions that allow comparison between studies and species.

Darrall and Jager (1988) examined a range of detailed tests that could be applied to air pollutant effects on plants, and concluded that great care had to be exercised if biochemical changes were to indicate pollutant stress responses. In particular, suitable internal or external controls had to be provided, and quantitative tests were generally not available at that time, with the exception of leaf reflectance and stress ethylene evolution. More recently, chlorophyll fluorescence has become a relatively simple non-invasive field of great potential use (Owens 1994). The variation between species, varieties and technique cultivars in their responses to particular pollutant and other stress combinations requires detailed information to be obtained on each taxon before biochemical techniques can be applied routinely (Darrall and Jager 1988). Nevertheless, it is important to incorporate some understanding of biochemical and physiological processes in more general indicators of plant responses to pollutants, and the following comments are provided towards this end.

(i) pH

Hydrogen ion or electron transfer is integral to the process of photosynthesis, so any factor that interferes with H^+ or e^- status will influence photosynthesis. The importance of environmental or substrate pH varies greatly with the size of plant studies, being a major determinant of the condition of lichens. Within plants, the indication of pH will depend on the precision with which tissues, cells or cell components can be separated and identified for analysis. Homogenised tissue samples will give only a general indication of the physiological responses to the presence of a pollutant (Roberts *et al*. 1981). Nieboer *et al* (1988) and Wellburn (1988) examined techniques for estimating intracellular pH changes in response to pollutant, and indicated that nuclear magnetic resonance and electron spin resonance were promising approaches, as they permitted non-invasive, repeated estimations of total and cell compartment pH. Whilst these techniques increase the understanding of metabolic processes and their responses to air pollutants, they are too time-consuming and expensive for use in monitoring, or even in routine experimental observation on whole plants.

(ii) Oxidation state

Several air pollutants, particularly ozone, sulphur dioxide and oxides of nitrogen, influence the oxidation state of cellular substances. The process of photosynthesis leads to the existence of O_2 concentrations adjacent to the mitochondria in the leaf cells that may be over 2500 times greater than those prevailing in mammalian cells (Scandalios 1992). These high O_2 concentrations are likely to result in the formation of superoxide ($\bullet O_2^-$) which, like hydrogen peroxide (H_2O_2), is very reactive, and results in the rearrangement of many substrates (Bennett *et al* 1988, Heath 1988, 1994, Hess 1994). The chemistry of superoxide regulation involves its conversion to H_2O_2 by superoxide dismutase, and breakdown of H_2O_2 by catalase, to water and elemental oxygen. In normal respiring cells, this oxygen is a useful substrate, but in actively photosynthesing cells, it must be eliminated, commonly by combination with phenols, sugars or amines (Hess 1994).

Scandalios (1994) indicated that, because superoxide is not transferred across membranes, antioxidant processes must occur within each organelle or cell compartment in which the superoxide is generated. The importance of this phenomenon from the point of view of tissue and organ function is that stresses may be very localised, with injury to physiological processes such as photosynthesis, or necrosis, scattered over the leaf (Heath 1994). Given the structural and chemical associations in photosynthesising leaves, it is not surprising that all of the most important air pollutants have oxidative properties. Further, the essential processes in plants inevitably give rise to conditions that increase the risk of injury from exogenous oxidative materials. Therefore, the capacity of cell components to avoid or tolerate these conditions is critical to the response of the whole plant

(iii) Ultrastructural changes

The close connection between cellular ultrastructure and biochemical function would lead to the conclusion that air pollutant stress will be associated with ultrastructural changes. Huttunen and Soikkeli (1988) reviewed some of these effects, emphasising that seasonal conditions provide a varying background against which pollutant effects must be assessed. For example, the composition of surface waxes varies with season, with lighter molecular weight fractions being lost during the summer, resulting in a change in wax conformation which may be accentuated by the presence of an air pollutant. These changes may influence the gas conductance of cuticle, and the rate of entry of pollutants through pathways independent of stomatal diffusion (Lendzian 1988). However, the process is not simply due to reconstitution of waxes on exposure to pollutants, as Jetter *et al.* (1996) demonstrated changes in wax composition occurred only at extremely high ozone and NO_x concentrations. It would appear that environmental conditions affecting other aspects of biosynthesis are more important in determining the changes in wax structure than the presence of oxidising pollutants.

Detailed discussions of the transfer of atmospheric pollutants to leaf surfaces, the composition and effects of pollutants on characteristics of leaf cuticles were collected by Percy *et al.* (1994). Taylor (1994) emphasised the importance of stomatal structure and function in determining the transfer of gaseous pollutants to sites of action within the leaf, and this view is incontestable for dry leaf surface conditions. However, there is also considerable concern over the accession of ionic species through wet leaf surfaces as a consequence of acidic precipitation, so that effects of pollutants on wax structure (Huttunen 1994), and cuticular permeability to water and pollutants (Kerstiens 1994, 1996, Tyree 1994, Reiderer *et al* 1994) have been examined. From isolated, pristine cuticles, the permeability to water appears to be unaffected by exposure to SO_2, O_3 or acidic precipitation, but the permeability to ions may be either increased or decreased by acidic precipitation. Intact leaves may show different responses (Kerstiens 1996), suggesting that metabolic conditions rather than the physical and chemical properties of the cuticle, may have important effects on leaf surface permeability. This uncertainty means that the steady state examination of conductivity on isolated cuticles may not be appropriate, particularly when surface damage causes major breaches in the continuity of the cuticle (Hoad *et al* 1994, Jeffree *et al* 1994). In addition, the permeability of *Picea englemannii* cuticles increases with leaf age and with the altitude at which the trees grow (Hadley and Smith 1994), suggesting that high-altitude communities may be more susceptible to uptake of water-soluble ionic pollutants. The importance of the environment on biosynthetic pathways and consequently on cuticular conductivity to water and pollutants was emphasised by Percy *et al* (1994), indicating that the conditions during leaf development as well as the immediate exposure conditions need to be described in order to understand species responses to air pollutant exposure.

Within the leaf, chloroplast structure has been shown to respond sensitively to all air pollutants that have been studied (Huttunen and Soikkeli 1988). Decreased chloroplast size, decreased granal size and dilation of the thylakoids, and granulation of the stoma have been reported. These changes are likely to impair photosynthetic function, due to the close dependence between chloroplast structure and function (Parry and Whittingham 1988, Wellburn 1988).

(iv) chlorophyll fluorescence

Chlorophyll fluorescence has been long-recognised as an important property of the photosynthetic system (Papageorgiou 1975, Krause and Weis 1991) and it has been used recently to characterise the potential of leaves to function under varying environmental conditions (Bolhar-Nordenkampf *et al* 1989, Schreiber and Bilger 1993). Some of the early procedures required temperatures of 77 ^{o}K, which precluded field use, but further examination of responses at ambient temperatures established that these could provide useful indications of intrinsic chloroplast functions. It is this recent development that is most applicable to pollutant studies, in that field investigations are possible, the procedure is relatively quick and repeatable, and an indication is given of the capacity for electron transport in Photosystem II (Mohammed *et al.* 1995).

(v) Enzymatic activity

Enzyme activity will be a resultant of the concentration of enzyme and its ability to function. Enzyme concentrations can be determined by their extraction and assay under standard conditions, and this is used widely in plant physiological research. However, *in vitro* assays of activity do not necessarily indicate the *in vivo* condition, as the enzyme may be inactivated or blocked by the presence of another enzyme or the absence of a suitable substrate.

Recent advances in enzyme detection, using immunological markers, enable *in situ* activities of enzymes to be demonstrated, and ultimately quantified. For research purposes, these advances are exciting, but for application to field monitoring, they are still an expensive and distant prospect.

4.3 Air pollution influences on seed yield and regeneration

4.3.1 Pollen and ovule production

Much initial work with air pollution effects on plants assumed that most effects on seed production would be indirect, resulting from changing patterns of photosynthate translocation, resulting from injury elsewhere on the plant, and moderated by the fact that developing seeds are, by definition, generally well protected from the outside environment. This, in turn, has led to an understandable tendency to concentrate on seed crop yield as a measurable indicator of pollutant effects. While this is a valid and important correlation, there are questions that yield observations alone cannot answer. Is decreased yield, for example, associated more with seed number or seed weight (quite different aspects of reproduction)? Is there an effect on seed viability? Is this effect due to air pollution interference with the mechanisms or pollination (perhaps indirectly through the behaviour of insect pollenisers, for instance)? Is there interference with one or more specific reproductive mechanisms? e.g. pollen tube growth, fertilisation etc. While concentrating on yield (and plant growth) effects is understandable (with pollen tube growth etc being so much harder to observe and measure) the effect may be to mask the nature of the true relationship between air pollution and seed development.

One example of this has been work carried out on winter wheat cultivars (Heagle et al 1979) where ozone was found to have a significant effect on seed growth and development, but with no consistent correlation to either visible foliage injury, plant growth or even overall yield.

Ozone has proven especially important in affecting seed development, generally, in a range of plants. This was first reported in 1974, with deleterious effects on both pollen morphology, ultrastructure and germination. Similar responses have since been found in a range of fruit, cereal and grain crops : typically with considerable variation between genotypes and ecotypes within even the same crop (Heagle et al 1979; Thompson et al 1976) and with effects extending to include loss of seed number, weight, size, rate of seed growth, and viability. Included in this list are a range of commercially-important food crops such as corn, maize, wheat, tomatoes, apricots, cherries, cotton and peanuts, as well as many forestry species.

As for the mechanism involved, this seems to be due to a combination of causes : direct effects on pollen grains exposed to high ozone levels (Cox 1987); impaired leaf photosynthetic function (sometimes); and altered assimilate utilisation. In some crops (e.g. tomato and cotton) seed (and fruit number) (Oshima et al 1979) are typically affected more than size. In other crops (e.g. soybean) (Endress and Grunwald 1985) both seed numbers and weight are all reduced. Part of this differential species response may be due to additional environmental factors such as water stress, temperature and radiation. These all affect seed development and are known to interact with various air pollution effects. Water stress, for example, can reduce the adverse impact of ozone on soybeans (Amundsen et al 1986). Air movement, high light, high temperature (3-30^{o}C) and even the use of pesticides can all increase 0_3 sensitivity.

A lot of the differences between species in their response to ozone and other pollutants can be explained with regard to their different mechanisms of photosynthate allocation (Cooley and Manning 1987). In seed crops such as wheat and peanuts the greater sink strength of developing seeds can maintain seed size despite widespread plant injury in general. This “self compensating” aspect of seed development in some species can complicate interpretation of pollutant effects. There may also be a “compounding” effect. Because of the priority given by many developing plants to reproductive development, a 10% increase in total carbon lost to respiration associated with air pollution injury and repair might result in a 15-30% reduction in ultimate seed yield, even if the relative partitioning of carbon amongst the plant tissues remains the same (Miller 1988).

Also difficult to quantify can be seed quality (rather than quantities) effects (Mulchi et al 1986). Independent of seed number and weight, for example, wheat grain protein content, particle size index, alkaline water retention capacity can all be adversely affected by ozone exposure : all detracting from subsequent flour making and baking quality. Somewhat less is known of the effects of ozone on forest, as regards to crop species, but adverse pollen production, pollen distribution, pollen germination, seed production, germination and flower initiation effects have all been reported.

Thompson, Katz and Cameron (1976) showed that, in two varieties of sweet corn, the number of ovules per inflorescence was not affected by exposure to ambient ozone-containing air as compared with filtered air. In tomato, Oshima *et al* (1975) found reductions in fruit number between 200 and 350 nl/l ozone, but it was not established whether this was caused by failure of floral initiation or later development.

The only other pollutant effects on seed production researched in much detail seems to be $S0_2$. Here the general effects on seed production seem very similar to those of ozone (Facteau and Rowe 1981) but with one unusual twist. At least for some seed crops in Europe (e.g. oilseed rape) a decline in sulphur emissions have been correlated with a lowering of yields, apparently due to sulphur deficiency (MacKenzie 1995). There is a further complication : sulphur compounds in plants also help defend against damage by oxidising chemicals such as ozone. Low level ozone pollution, which has replaced acid rain as the prime suspect in the death of European forests, is on the rise, just when plants have less sulphur to combat it.

Some plants have been shown to be especially sensitive to ozone (alfalfa, barley, bean, red and white clover, grape, oats, potato, radish, soybean, tobacco, wheat, ash, aspen, black cherry, tulip poplar, white pine) (Krupa 1996). This work still only relates to physical injury and yield effects, however and not to specifics of seed production.

It may also be necessary to separate out “acute” and “chronic” responses to air pollution. Acute responses (involving rapid physiological/biochemical changes) are known to be induced by relatively high hourly pollutant concentrations from a few to several hours on a given day (or recurring days) and the injury symptoms appear within a few to several days after exposure. Chronic effects, in contrast, are due to exposure to gaseous pollutants for much longer periods : whole growth seasons or even entire life cycles. Both acute and chronic responses to ozone appear to be due to moderate or intermediate, but not the highest hourly pollutant concentrations (Tonneijck and Bugter 1991; Grunhage et al 1993; Krupa et al 1993; Krupa et al 1995) (as used, at least in part, by current MfE guidelines).

Much pollution-monitoring concentrates on short-term acute effects and visible damage. These may or may not lead to subsequent crop yield reductions. Chronic exposures however, even if relatively low hourly pollutant concentrations, with periodic, intermittent, highly variable episodes can all affect less obvious factors such as retarded flowering, abscission, yield, seed development and altered nutritional quality and economic importance. It is such chronic effects that are therefore of most concern for agriculture and horticulture, particularly since these important effects can occur without attendant foliar symptoms. Since the total exposure period is also critical, long lived forestry crops (80-100 year rotation) may be adversely affected by even a very low ozone or $S0_2$ concentration, harmless to a short-term annual crop (WHO, 1987). While $S0_2$ pollution is often on a small, localised scale (causing acute symptoms), ozone, in particular, is likely to be more regional, even global in distribution, and therefore more of a chronic problem. $S0_2$ concentrations are also often found to vary seasonally, 0_3 levels to vary daily. Since tropospheric 0_3 production is primarily photochemical, high 0_3 levels are observed during daily periods of high radiation. This complicates the joint problems of monitoring, assessment and prediction.

4.3.2 Pollen distribution (vectors and their sensitivity)

Pollen distribution in wind-pollinated species (e.g. grasses and cereals) will not be affected by atmospheric composition, but the attraction of insects, birds and animals to flowers may be influenced by changes in colour due to floral bleaching, or nectar production due to a reduction in photosynthetic activity. There is no information available directly on these processes, suggesting that this aspect of reproduction is not markedly more sensitive than others that have been studied already.

4.3.3 Pollen tube growth and fertilisation

Floral fertilization in most species requires the pollen to germinate on the external surface of, and then grow into the receptor organ. This process exposes a single cell with high levels of metabolic activity to the external environment, making it potentially one of the most sensitive stages of plant development.

In conifers, pollen germination is associated with the appearance of a small drop of sap at the entrance to the micropyle of the ovary. The pH of this droplet appears to be influenced by the pH of both the soil and atmospheric depositions (Cox 1989), so that *Pinus strobus, Betula Alleghaniensis* and *B. payrifera* pollen germination *in vivo* was suppressed by 50% between pH 3.6 and 2.8. A similar, but less dramatic effect occurred in *Pinus resinosa* and *Populus tremuloides*. Venne *et al.* (1989) reported reduced pollen germination and pollen tube growth in *Pinus sylvestris* when the pollen grains were exposed to sulphur dioxide or ozone. Clonal differences were observed in these responses, and the contribution of the pollen parent to successful fertilisation under polluting conditions varied from 0 to 35%, .

Fluoride also reduces pollen tube growth, and consequently seed set in tomato and cucumber (Sulzbach and Pack 1972) and strawberry and peach (Bonte *et al.* 1981, 1982). These effects occur through interference with calcium metabolism (Bonte *et al.* 1982), and cell wall formation, a response that has consequences for the growth of all tissues.

4.3.4 Seed yield (number and size of seeds)

Thompson, *et al* (1976) showed that seed yield in two varieties of sweet corn was decreased significantly by exposure to ambient ozone-containing air as compared with filtered air, with almost complete failure of ovule set in the terminal portion of the inflorescence of one variety. This response was linked with foliar injury to one variety and the resulting loss of photosynthetic capacity. Other studies (Table 2) have indicated that significant reductions in fruit or seed weight in several species occurred first at ozone concentrations ranging from 0.06 to more than 0.35 ppm. The responses of different attributes varied considerably, a conclusion reached by Cooley and Manning (1987) from studies on 10 agronomic species. This variation in response makes extrapolation of existing data to new situations, such as New Zealand plant species, difficult, but inevitable.

Table 1: Concentrations at which air pollutants first reduce fruit growth in selected agronomic species.

Pollutant	Species	Attribute	Concentration ppm	Reference

Ozone	Wheat	Seed weight per plant	0.06-0.10	Heagle et al 1979
		Individual seed weight	0.10-0.13	
	Tomato	Leaf and stem weight	0.20	Oshima et al 1975
		Immature fruit weight	0.20-0.350	
		Mature fruit weight	>0.35	
		Number of fruit per plant	0.20-0.35	
	Cotton	Number of bolls	<0.25, 13 weeks	Oshima et al 1979
		Boll dry weight	<0.25, 13 weeks	
		Fibre dry weight	<0.25, 13 weeks	
		Fibre % in boll	>0.25, 19 weeks	
	Soybean	Pod number per plant	> 0.097	Endress & Grunwald 1985
		Filled pods per plant	0.046-0.07	
		Seeds per plant	0.046-0.07	
		Seed weight per plant	0.046-0.07	
	Soybean	Pod weight (watered)	0.090-0.13	Amundson et al 1986
		Pod weight (droughted)	>0.13	
		Pod number (watered)	>0.13	
		Pod number (droughted)	>0.13	

4.3.5 Seed germination and seedling establishment

Germination of non-dormant seeds is controlled largely by the soil environment, and particularly by the availability of water, oxygen and appropriate heat. Ions in the soil solution may influence germination through osmotic or direct ionic effects, so that air pollutants that are deposited on the soil may influence germination. In most situations, the rate of addition of a pollutant to the soil solution is likely to be low, but progressive additions of acidic precipitation will lower soil pH, sulphur concentrations may increase, also influencing pH.

If gaseous pollutants are removed from the atmosphere by wet scrubbing systems, and the waste liquor is applied to the soil or waters, the resulting solution may contain sufficient pollutant to inhibit germination. For example, soluble fluorides may be present in sufficient concentration to reduce germination, through both osmotic effects, and also through the effects of fluoride on calcium metabolism and cell wall growth. The areas over which this phenomenon would apply are likely to be small, but may be important locally.

4.3.6 Seedling vigour and competition

Seedlings may be more sensitive to pollutants than are more mature plants, as in the case of fluoride exposure in many species (Weinstein 1978). Alternatively, plants may not become susceptible to injury until they have reached a certain size, and a certain stage of leaf maturity, as in the case of ozone injury in tobacco. Therefore, the effects of pollutants on seedling growth are likely to be similar in general outcome to the effects on mature vegetative plants.

4.4 Functional diversity and stress responses of populations

There is a longer-term effect on air pollution on reproduction and seed yields to be considered also. That is the response not at the individual plant level, but at the population level. Where air pollution concentrations are high, there will be strong selection pressure applied on individuals to avoid, tolerate or compensate for pollutant effects. This will be especially true if the effects are felt directly on yield, seed production and reproductive behaviour. There is considerable variability in individual responses to air pollution stress. Differences in population sensitivity to ozone (and the interaction between ozone and $S0_2$) have been clearly shown in a range of forest species (reviewed in Thompson et al 1976; Oshima et al 1975; Ormrod and Hale Marce 1990). Various authors have observed viability selection, fertility selection, genetic drift and mutation occurring in response to pollution pressure (reviewed in Degen and Scholz 1998; (WHO, 1987.). Changes in the distributions of genetic types (alleles and genotypes); loss of genetic multiplicity; and changes in genetic variations, either at the individual or population level (heterozygosities and genetic diversities) have all been observed. Such specific genetic parameters can now be monitored by means of enzyme gene markers. Such genotyping may represent an increasingly important means of studying future pollution and environmental impacts (Scholz et al 1987). The extent to which any of these processes may endanger the stability of otherwise long lived ecosystems however, is still a matter of debate. This has led to the development of simulation models such as “Eco-gene” (Degen and Scholz 1998) designed to investigate possibilities such as more sensitive species being eliminated, giving way to more tolerant (but perhaps less desirable) competitors, thus changing the sociobiology of the ecosystem. Interestingly, this may often show no obvious correlation with visible symptoms. And, while a clear case can be made for the evolution of resistance to $S0_2$, over time, there is, as yet, only limited evidence of similar natural selection for ozone tolerance.

In forest poplar and *Pinus* spp. $S0_2$ and 0_3 have produced detrimental effects on anther development, pollen germination, pollen growth, seed germination and seed growth. Most importantly, these effects varied between different clones, showing the potential for fertility selection in natural tree populations. The natural buffering capacity of the stigma surface also helped modify some of these effects. Consequently, timing was especially important, with different phases of flowering and pollination proving differentially sensitive to atmospheric pollution. This, again, makes the determination of critical pollution thresholds difficult. Typically though, the concentrations reportedly required to produce this sort of damage have been quite high (340 μg $0_3/m^3$; 170-270 μg m^3 of $S0_2$), and in various *in vivo* studies higher rates have been required, again, compared to *in vitro* tests. Why this should be so remains unclear (Scholz et al 1987).

Other gaps in the knowledge base concerning the possible genetic effects of air pollution on natural ecosystems are:

i) base-line data on "normal" genetic multiplicity in natural ecosystems

ii) actual mechanisms by which genetic damage may occur

iii) a means of quantifying the effects

and, iv) strategies to conserve remaining gene resources if problems are identified

At the moment it is often difficult to prove detrimental effects specifically due to any specific reduction in genetic multiplicity (Scholz et al 1987).

What may be especially useful in this, and other, studies however, are indicator species of known tolerance or sensitivity to selected pollutants. Beans, clover, fir and spruce are especially sensitive to $S0_2$ (oak and pine especially tolerant); annual ryegrass, morning glory, spinach and some tobacco species are especially sensitive to ozone. Their further development and use as bioindicators of environmental quality, ecosystem stability, (or degradation) could help overcome some of the "technical" assessment problems summarised above.

4.5 Selection pressure from pollution

Plants, in particular trees, are significant interceptors of air pollution in most ecosystems. Plants are effective gas exchange systems, with the exchange occurring mostly (in higher plants) via stomata, as the epidermis provides a protective barrier through which very little uptake occurs.

Trees are long-lived sessile organisms. The significance of this is that, in order to survive frequent changes in their environment, they must achieve a balance between sufficient adaptedness to the prevailing environmental conditions, and enough genetic potential to be able to adapt to future environmental conditions. This is essential to ensure stability of forest ecosystems. Individuals, as well as the population, need to possess high genetic multiplicity (Gregorius, 1989, Ipsen et al 1998, Degen and Scholz, 1998). Many studies have shown that forest trees have a higher degree of genetic variation than other organisms which are either mobile and can escape adverse environmental conditions or are short lived.

4.5.1 Ideas related to survival and 'selection'

Large natural populations are likely to have many genotypes with differing sensitivity to an environmental stress. Gregorius (1989b) posed two questions concerning the understanding and management of air pollutant effects on plants, and particularly on forest trees: (1) the nature and extent of the effect of the environmental stress on a plant, and the variation between plants in a population; (2) if variation exists, does it lead to successful adaptive processes? While the first questions has been investigated extensively, there is comparatively little information on the second, even though this may be more crucial to the maintenance of species in an inexorably changing environment. Gregorius (1989b) used adaptation to indicate both a general condition which represents the capacity of a species to survive and reproduce under changing environmental conditions, and a particular trait of a species which enables it to survive under defined conditions.

4.5.2 Selection between individuals

Where a new stress is imposed on a population, the existence of variation in the population provides the basis for evolution, in that a failure to evolve (survive) can be argued to "only be due to lack of the appropriate variation" (Bradshaw and McNeilly 1991). They point out, however, that survival requires possession of variation appropriate to the stress in question, whether it is disease resistance or pollutant tolerance. They also indicate that mutations are random in their occurrence in a population, but not in their direction, so that some species may not have the genetic capacity to mutate in a way that increases tolerance to a particular stress.

Bradshaw and McNeilly (1991) indicate that selection may depend on small differences between the fitness of individuals for a particular environment, and that the critical difference may be difficult to demonstrate statistically. The differences may be associated with stress tolerance directly, or with general plant vigour, which can be influenced by stress tolerance (Tingey and Andersen 1991). Bradshaw and McNeilly (1991) suggest that, where resistance shows continuous variation within a population, changes in the population occurs in three stages: (1) elimination of the most sensitive genotypes; (2) elimination of all except the most resistant genotypes; (3) interbreeding of the survivors, resulting in more resistant genotypes.

4.5.3 Selection between species

Species clearly differ in their intrinsic physiological tolerance of environmental stresses, due to the entire range of characteristics discussed in this review. They also vary through possession of different life history traits, including longevity, most common mode of reproduction, perennation mechanisms (storage organs), seed banks, phenotypic plasticity, and life form (Barrett and Bush 1991). These traits, which may be revealed by molecular techniques (Cullis 1991), combine to produce widely differing resistances, rates of growth, and rates of dominance in mixed populations (Bradshaw and McNeilly 1991), because the functional characteristics and relative populations of species influence genetic structure of each species, while mating systems influence the amount of genetic recombination (Barrett and Bush 1991). Resistance is likely to develop only where there is sufficient heritable variation in a species to grow and reproduce in a given environment (Muller-Starck 1989). This has important implications for the maintenance of diversity in plant populations, and thus the maintenance of sufficiently large contiguous areas of natural plant communities. If pollutant resistance is a multigenic effect, Barrett and Bush (1991) conclude that the evolution of resistance becomes a case of directional selection on a quantitative trait.

One of the most interesting questions regarding selection is its extent in environments where the level of pollutant stress is relatively low. Barrett and Bush (1991) indicate that the most rapid evolution is likely to occur in short-lived herbaceous species, and slow in long-lived outbreeding species with seed banks. Because of the genetic structure of tree populations, changes in their populations in response to environmental stress are likely to be slow, but trees have a higher level of genetic diversity and heterozygosity than other life forms, so their capacity for adaptation may be relatively high (Gregorius 1989b). In addition, this variation may be associated with genetic information that is redundant under normal conditions, and which is retained at some energetic cost (Winner *et al.* 1991). The long life span, and considerable degree of phenotypic variability in trees may require such energy-inefficient characteristics, although under widely varying environmental conditions this apparent inefficiency may be highly effective for survival.

Severe pollution would be expected to simplify the population structure, but there is no detailed information on the extent to which relatively low levels of pollution influence the genetic structure of plant populations. From the foregoing discussion, if the population is sufficiently large and the original structure is maintained, evolutionary change towards increased pollutant resistance could be expected, but only after several generations. An example of this is provided by Mejnartowicz and Palowski (1989), who demonstrated that four populations of *Pinus sylvestris* from unpolluted areas of Poland were genetically similar, but two populations from a heavily polluted area were very different from both the unpolluted populations and each other.

4.6 Aspects of Forest Decline

4.6.1 Definition

The term *decline* is a general description for the progressive worsening of forest stands. The term implies long-term damage and a progressive deterioration in tree condition. *Dieback* is also often used and refers to the death of branches from their tips back towards the main stem often in the upper crown (branch dieback). Although dieback is typically used for single trees it is also often used for stands so that the terms can become confused. Decline is used here for stands and dieback is the typical process involved at the tree level. Decline symptoms can very in severity and sequence between species.

4.6.2 Typical symptoms:

Silver fir (Abies alba Mill.)

- chlorosis and yellowing of needles, mainly upper side and starting at base of crown.
- casting of older needles, starting from the base of branches
- premature reduction in height growth relative to side shoots giving rise to stork's nest formation
- reduction in fine root system

Norway spruce (Picea abies (L) Karst.)

- severe yellowing (typical magnesium deficiency) at base of crown and loss of older needles and death of secondary shoots in upper crown
- formation of recovery shoots on the upper side of the affected branches- drooping of branches and twigs
- reduced fine roots and mycorrhiza

Kaimai Range forests (Nothofagus spp., Ixerba brexioides, Beilschmiedia tawa)

- chlorosis of leaves, in particular one-year old leaves.
- scorch and other marking of leaves
- leaf fall, especially of older leaves
- dieback of twigs
- mortality of all tree species in affected area

In all cases there is a marked fall in tree growth rate, especially in diameter growth, which can precede visible symptoms by many years.

Major public concern arose in Europe in the early 1980s when surveys revealed substantial damage in a wide variety of forests. In 1982 a survey in Germany suggested that 8% of forests were damaged and this increased to 34% in 1983 and 50% in 1984. These figures have since been extensively challenged when it was discovered that forests often show substantial damage at the individual tree level even when perfectly healthy. For instance, a normal tree can have up to 25% of leaves or twigs damaged and, superficially, appear unwell. Perhaps one of the most important results of recent research on declines has been a much better understanding of how a normal forest functions.

4.6.3 Suggested causes

The following four hypotheses have been proposed to explain forest decline Uhlmann et al. 1989):

1. natural causes (climate) and epidemics.

2. direct effects of air pollution on above ground plant organs.

3. mineral deficiencies and imbalances as a consequence of acid deposition and soil acidification.

4. various combinations of these factors.

4.6.4 Actual Causes

There have been several substantial research projects investigating declines in both USA and Europe. It was soon discovered that declines were a complex situation and not easily understood in terms of simple cause/effect models.

Red spruce decline, USA (Johnson et al. 9). Direct effects of pollutants such as sulphur dioxide and ozone were not found. Cumulative effects due to acidic deposition were the likely cause. Acid deposition caused leaching from leaves and, due to aluminium release, reduced calcium uptake by roots. This led to poor growth performance in lowland stands and an unexpected decline in cold resistance in upland stands. Red spruce was found to be close to its tolerance limit with respect to cold and increased respiration due to lowered calcium produced reduced carbohydrate stores and loss of cold tolerance. The trees were then killed by cold periods in winter.

Spruce, Fichtelgebirge, Germany (Schulze et al. 1989). Again, a direct effect of air pollutants was not found and the decline was best explained by a changed calcium to aluminium ratio in the soil and a reduced uptake of magnesium. This was compounded by an increased supply of nitrogen from atmospheric deposition, also from industrial sources, that prevented the normal tree response to low nutrients, ie: reduced growth rates, and forced the trees into severe nutrient stress and eventual death.

4.6.5 New Zealand declines

Forest declines are well known in New Zealand and have been reported in several locations. Beech (*Nothofagus* species) decline occurred at National Park in 1960s or 1970s (actual date unknown) and is reported to have also been present around the beginning of the century. A general decline is known from high altitude forests in Kaimai Ranges (Jain and Green 1983) and a rata (*Metrosideros* spp.) decline is known for the West Coast and other areas. The most heavily researched decline is that of the Kaimai Ranges. This affected all species of trees above a certain altitude which differed between locations. The predisposing factor appeared to be cloud formation over the ranges which led to high soil water content and reduced root system formation. This left the trees sensitive to droughts with rare, severe events leading to forest collapse. The decline had occurred several times over the past three centuries and was linked to changes in climatic conditions.

Declines in New Zealand all appear to be natural events similar to those reported else where in the world (Huttl and Mueller -Dombois 1992) and not to be linked to any pollution.

4.6.6 Manion hypothesis (Manion 1981)

The above examples reveal both the complexity of a decline situation with respect to pollutants, in particular the absence of any direct effect on the plants, and the importance of time sequence in the development of the decline. Manion (1981) produced an overview that is generally applicable to declines and which provides an excellent framework for any interpretation, both of existing and new declines.

Three stages are proposed which occur in sequence.

1. *Predisposition*: Trees become weakened and thus predisposed to damage through one or several conditions linked to their growth site ie: location is important. Such conditions can be abiotic or biotic but are chronic, not acute, and cause reduced growth but few other obvious symptoms. Low nutrients, exposure, poor soils, pollutants would be typical chronic but sublethal causes. The net result is a tree with reduced internal reserves and a lowered ability to respond to any severe event.

2. *Inciting event*: this is typically a severe, abiotic event that leads to dieback and loss of biomass by the trees. Drought is the most common inciting event but defoliation by insects is a possible biotic alternative. The result is a need for the tree to commit all reserves to the recovery process.

3. *Contributing*: At this stage a large number of opportunistic weak pathogens can invade the tree and lead to eventual death. The tree shows strong symptoms and this is usually the stage when the decline is recognised and public interest occurs. It is also a stage at which recovery is usually not possible and complete forest loss can occur.

The time sequence of the events is crucial and the long predisposing stage can completely hide the actual underlying causes of a decline. Causes can be natural, silver fir declines in Europe have been known for centuries with the species having reached its maximum in the 1600s, but the contributory effect of any pollutants is also clear.

4.6.7 Risk assessment for pollution induced declines in New Zealand

All existing declines in New Zealand are the results of natural processes. In the northern hemisphere examples which have been well and extensively researched the important factor has not been acute damage by the pollutants but a steady supply over a long period. This leads to some form of ion imbalance within the tree and eventual death following the fall in resources along the Manion sequence. It is worth, therefore, comparing the level of atmospheric deposition in New Zealand in comparison to that in decline affected areas elsewhere. In Table 1A, B and C the mean annual inputs by bulk rain, and the ion compositions of rain and fog are compared between New Zealand South Island sites (Verhoeven et al. 1987) and sites in Germany and USA (Eiden 1989).

It is clear that, for all ions both as composition and annual input, that overseas inputs and compositions are over an order of magnitude greater than in New Zealand forests. It is unlikely, therefore, that pollution induced forest decline would be expected to be a problem in New Zealand except in areas receiving unusually high inputs. It is possible that such areas do exist in the neighbourhood of large cities like Auckland but substantial modelling and a measurement programme would be needed to identify the sites at risk.

The one exception to this generalisation is ozone. No data seems to be available for at risk forests like those of Coromandel, downwind from Auckland, and it is faintly possible that some general forest effect could be occurring.

Table 2: Comparison of ion contents of bulk rain and cloud and deposition rates by bulk precipitation between European, North American and New Zealand sites.

A. Mean annual input with bulk precipitation (10^{-3} mol m^{-2} a^{-1})

Site	SO_4-S	NO_3-N	H^+	NH_4-N
Fichtelgebirge Germany	73.4	72.1	60	63
Hubbard Brook USA	40	32	97	16
Maimai New Zealand	<2	1.1	0.8	<3

B. Fogwater composition (µeq l^{-1})

Site	pH	SO_4^{2-}	NO_3^+	NH_4^+
Fichtelgebirge Germany	3.0	1600	640	860
Whiteface Mt, NY, USA	4.2	140	110	89
Craigieburn New Zealand	6.1	-	5.1	18

C: Ion concentration of bulk precipitation (µeq l^{-1})

Site	pH	SO_4^{-2}	NO_3^+	NH_4^+
Fichtelgebirge Germany	4.2	164	82	73
Hubbard Brook USA	4.1	60	24	12
Maimai New Zealand	5.6	<3	0.4	<3

4.7 Effects of fluoride on vegetation

Fluoride is one of the most toxic of the common air pollutants, as it exerts effects at concentrations about ten times lower than those of the more common pollutants (Weinstein 1978). However, its importance as an air pollutant of serious concern has diminished during the past decade or two, principally because of the development of improved technologies for its containment in manufacturing processes and its removal from waste gas streams. These developments have been most prominent in the aluminium smelting (reduction) industry, in which the fluoride-containing mineral cryolite is used as a flux, and hydrogen fluoride is produced as a result of high temperature electrolysis. Modern smelting techniques can retain in excess of 98% of the fluoride generated within the process equipment, and can retrieve in excess of 99% of the fluoride in the gas stream and return it to the process. Aluminium smelters continue to be of environmental interest because of their large size and the total quantities of fluoride they emit.

Other industrial sources of fluoride include phosphate fertiliser works, where fluoride is released during the acid treatment of phosphate rock, brickworks and glass factories, where fluoride is produced by heating fluoride-containing minerals, and the burning of coals containing fluoride. In the main, these industries are smaller mass emitters of fluoride than aluminium smelters. With the exception of large coal-fired electric power stations, the waste gases are limited in volume, are emitted at relatively low altitudes, and usually affect local areas.

As a result of the technical improvements in aluminium smelting, the amount of research on fluoride and its effects on plants has decreased greatly in the last 20 years, so that the review by Doley (1986) still represents a current perspective of the field with respect to a number of species occurring in New Zealand. Fluoride effects on New Zealand vegetation have not been studied extensively apart from field investigations associated with the aluminium smelter at Tiwai Peninsula.

Fluorine is not known to be an essential element for plant nutrition, but it may be accumulated from either the air, where it occurs mostly as hydrogen fluoride, or from the soil, where it is highly soluble in water and moves as a simple halide anion (NRC 1971). Its chemical properties result in its extensive combination with divalent cations to form compounds of low water solubility, resulting in low soil solution concentrations of fluoride unless the soil has a low buffering capacity (Doley 1986). Consequently, fluoride is regarded as an atmospheric rather than a soil pollutant, and its uptake is regulated by the gas transfer processes between the air and the wet cell walls within leaves. This labile fluoride may be lost from the leaf again by volatilisation and diffusion through the stomata into air with a low fluoride concentration. Within the leaves, it is carried in the transpiration stream to the extremities of leaves, or it diffuses into cells and accumulates in organelles. It does not appear to be transported in large quantities in the phloem of plants, so that redistribution from leaves to other organs is limited.

Fluoride is a potent ion, combining with calcium and magnesium and thereby interfering with their metabolism in such processes as chlorophyll formation (magnesium) and cell wall synthesis (calcium). These characteristics lead to some of the most sensitive visible injury symptoms of chlorosis and deformation of expanding leaves in susceptible species. Fluoride also reacts with cell membranes of various descriptions, and some enzymes. Interference with cell wall growth may be particularly marked in the pollination process, leading to failure of fertilisation and fruit development (Bonte 1982).

Unlike most of the other atmospheric pollutants, fluoride in an accumulative toxin that affects tissues at average concentrations as low as 20 μg/g. The concentrations at the cellular level associated with these overall tissue concentrations are not known, although the fluoride concentrations in parts of leaves showing fluoride injury may be up to 20 times those in uninjured portions (Garrec *et al.* 1972).

Because of redistribution within leaves, accumulation in forms that may remain chemically active, and lack of metabolic requirement, the accumulated dose of fluoride is important in determining exposure, even though there is a sensitive response to increasing concentration during any exposure. However, the relationship between either fluoride exposure or fluoride concentration in tissues and the effects on different processes within plants varies considerably both between and within species. In particular, the associations between physiological and growth effects, and the associations between these effects and visible injury vary even more (Doley 1986). Consequently, great care needs to be taken when generalising on the responses of plants to fluoride exposure.

Another area of concern in evaluating fluoride effects is the similarity of symptom expression between fluoride and a number of other environmental stresses that result in tissue necrosis or chlorosis. Commonly, these symptoms are so similar that great care must be taken in determining the extent of fluoride injury.

Investigations into the responses of New Zealand vegetation to fluoride suggest that the range of fluoride sensitivities is similar to that found in other regions (Doley, unpublished). This finding corresponds with that for Australian species, where the range of sensitivities was very similar to that described in north America (Doley 1986). It is not possible to predict which species might be most sensitive, and although plants with large leaves tend to be sensitive, plants with small leaves are not all tolerant. Life form and taxonomic grouping are not necessarily reliable guides to fluoride sensitivity, with sensitive and tolerant species being distributed between large and small plants and between conifers and angiosperms.

The ANZECC guidelines for fluoride in air are regarded as adequate for the protection of vegetation, particularly as three categories of land use were recognised.

5. ASSESSMENT CRITERIA

Physiological tests applied routinely to plants in order to estimate their condition or responses to stresses should posses several characteristics. Mohammed *et al.* (1995) examined methods for determining the physiological condition of tree seedlings prior to field planting. Whilst the plant attributes of greatest interest for forest establishment are not identical to those for assessing the response of plants to pollutant stress, the criteria for assessment can be adapted to pollutant effects research and monitoring. The scheme of Mohammed *et al* (1995) is produced in Table 1, with modification of the Speed of Assessment and Applicability to Monitoring categories.

Table 3: Criteria that may be used to assess field response of plants to air pollutants (after Mohammed *et al*. 1995)

Characteristic	Weight	Ranking criterion
Speed of Assessment	3 2 1	< 1 h < 1 day > 1 day
Simplicity	3 2 1	anyone can use requires technician requires scientist
Cost	3 2 1	< US$100 US$100-1000 >US$1000
Reliability	2 1 0	very reliable reliable not reliable
Sample disturbance	2 1 0	no damage partial damage specimen destroyed
Quantitative	2 1	results can be analysed statistically qualitative analysis only
Diagnostic utility	2 1	able to determine cause of problem not able to determine cause of problem
Basis of measurement	2 1 0	physiology is measured directly physiology is inferred non-physiological assessment
Adaptability	3 2 1 0	useful for more than one function and season useful for more than one function useful at more than one time useful at one time in the growing season
Predictability	3 2 1 0	high predictability of future condition and long prediction span highly predictable somewhat predictable not predictive of future condition

Applicability to Monitoring	3 2 1 0	highly useful for monitoring moderately useful slightly useful not useful

For the determination of tree seedling condition, chlorophyll fluorescence was ranked the highest, closely followed by photosynthetic gas exchange, the differences being the relative simplicity and diagnostic ability of the chlorophyll fluorescence approach, and the greater adaptability of gas exchange. Mohammed *et al* (1995) indicated that sampling procedures must be determined very carefully, and where plants are growing in highly polluted environments, the ambient conditions may be unsuitable for sensitive instruments (Saarinen and Liski 1993), attention must also be paid to sample storage and pre-treatment.

6. BIOMONITORS OF AIR POLLUTION

In general, biological monitoring has great popular appeal, being perceived as a very sensitive, easy, economical, readily available or easily comprehended means of determining the presence, the quantity or the effect of a pollutant in the environment. These characteristics of biological monitoring need not be mutually exclusive, but neither are they always congruent, and it is important to recognise that determination of a pollutant impact on complex biological systems is rarely simple, rapid, unequivocal, convenient or inexpensive (Zonneveld 1983, Jeffrey and Madden 1991).

For many members of the public, the combined effects of all pollutants may be more important that the effects of each constituent of a pollutant mixture. For emitters, the effects of the pollutant for which they are most responsible will be of principal concern. Regulators may be interested in biological monitoring as a supplement to other means of pollutant assessment. These three social groups are likely to have very different, and possibly irreconcilable requirements of biological monitoring, so an acceptable technique or techniques must be developed for clearly defined purposes.

Several requirements for implementation of biological monitoring may be summarised as:

1. Definition of the purpose of environmental description;

2. Recognition of attributes of the species that influence their utility as monitors;

3. Identification of the most reliable and efficient means of collecting and analysing the required information.

6.1 The Purpose of Biological Monitoring

The most important step in establishing a program of biological monitoring is to identify the purpose of sampling, as this must justify all subsequent steps. Smith (1994) identified four purposes of biological monitoring related to pollutants which included advance warning of threats to other species, and detection of episodic emissions of pollutants. These purposes are clear, but may be more restrictive than is desirable for wide application to terrestrial environments. Four purposes of routine biological monitoring that include those presented by Smith, but express concerns in a more general manner are:

1. to estimate ambient concentrations of a pollutant;

2. to protect ecosystem health and environmental well-being through indication of the risk of significant harm to certain species;

3. to prevent significant harm to an existing commercial activity through indication of the risk of significant harm to that activity;

4. to establish a historical record of a biological parameter.

Continual testing of the assumptions and methods of biological monitoring is essential if biological monitoring is to be useful to society (Ramamoorthy and Baddaloo 1991), as every organism is affected by many environmental factors, and not only by the component that is the objective of monitoring. The separation of these interacting factors is often difficult, but it is critical to the reliable development and application of biological monitoring.

6.2 Biological Indicators of Pollution

A wide range of organisms can be utilised for indicating the pollution status of an environment. The method can be Active, where the organisms themselves or the structure of the community can be correlated to pollution levels, or Passive, where the properties of organisms to take up and sequester substances is used to monitor the substance abundance.

Typical examples are:

- Lichens, both active and passive,
- Bryophytes
- marine algae
- macroinvertebrates in streams
- macrophytes in streams
- birds

Normally these are active monitors and the organism has to be analysed for the presence of a pollutant and this level has then to be calibrated against ambient values. Use of the organisms depends on the availability of a specialist to obtain identifications and on finding a means to relate either absolute content or community structure to surrounding pollutant levels. Sometimes it is easier to use the organisms as living monitors and to analyse them only to detect the extent of a known pollution event. In general biological indicators are very cost effective in comparison to sophisticated mechanical apparatus however, it must be accepted that they cannot replace such equipment when real values are required.

6.3 Examples of biological indicators

6.3.1 Lichens

Lichens are poikilohydric symbioses between a fungus and a photosynthetic partner, either an alga or a cyanobacterium. They typically grow on substrates such as bark or stone and receive most required nutrients from the air. They have exceptionally good uptake systems and this makes them both sensitive to pollutants and also excellent accumulators. Thus it is normal to either use lichens by analysing community structure or by analysing the plants themselves for contents.

Although sensitive to many pollutants, lichens are especially well known for their sensitivity to sulphur dioxide. SO2 was produced in great quantities by generating stations and was a major pollutant in industrial zones of the north until recently when legislation forced a cleanup of stack gases with a consequent improvement in air quality. The classic work of Hawksworth and Rose (1976) produced a 10 zone classification that links the presence or absence of lichens to mean ambient SO2 concentration.

Zone	Moderately acid bark	Mean SO2
1	algae only at base of tree	>170
2	Algae spread,	150
3	L. conizaeoides very common. Lepraria aprina appears.	125
4	Hypogymnia physodes, P. saxatilis	70
5	H. physodes extends further up trees an	60
6	Parmelia caperata. Usnes impolita	50
7	P. caperata and Usnea spp.	40
8	Usnea sp + Parmelia reticulata	35
9	Lobaria sp appear.	30
10	Lobaria, Sticta and sensitive groups like Usnea florida.	Pure

This table is based on European lichens and, therefore, is not easily applicable to New Zealand since some species ill not be present.

The attached table lists lichens that have been rated for pollution sensitivity in Europe that are also present in New Zealand. Name changes and additions to the flora have prevented an exact identification in some cases. In the table the sensitivity value is the number of the most polluted zone in the table above in which the lichen can be found.

Unfortunately many of the species are rare but there are a large number which are found mainly on the bark of introduced trees and these could be potentially useful because such tree species are typically planted near or in cities.

The actual application of the zone system is difficult because it requires a very high degree of taxonomic expertise which is not normally available. Zonation does appear around Christchurch but, in Hamilton, lichen species characteristic of "pure" air are found on street trees within one kilometre of the city centre. This draws attention to the much lower SO_2

pollution in New Zealand. This is a result of the much lower population density and fewer coal-burning power stations. When a check was made around the very dirty, but small Meremere power station SO_2 sensitive lichens were found in its immediate vicinity whilst it was in operation.

Physiological indications: considerable effort has gone into finding a more rapid method of using lichens as indicators. Methods of measuring rapid changes in photosynthesis (eg: chlorophyll fluorescence, Gries et al. 1996) are promising but require considerable equipment and personnel to monitor a situation. Alternatively, sensitive lichen species can be transplanted into an area suspected to be polluted and the consequent effects monitored. This is good for point sources (Galun and Ronen 1988) but still requires much effort.

Sensitivity of New Zealand species: it is possible that lichens, and other plants as well, in areas that have always had low pollution levels could be more sensitive than northern hemisphere equivalents which have suffered selection over many hundreds of year. This is a relatively unresearched but important question. Limited comparisons in Ireland (Richardson 1981) suggest lichen species to be sensitive to a third of the pollutant levels as samples of the same species in England. No data is available for New Zealand species but student studies at Waikato University suggest the lichens to be much more sensitive than in Europe.

Lichens and bryophytes as absorbers: a more powerful methodology is to capitalise on the excellent absorbing capacity of lichens and the other major poikilohydric group of plants, the bryophytes (in particular mosses). In this system samples are displayed in some way, mosses in bags are normal but transplanting is preferred in lichens, for a period of time and are then analysed for increased levels of pollutants. This is highly effective and have revealed considerably enhanced levels of pollutants near sources overseas eg: sulphur around a smelter in Canada (Nieboer and Richardson 1981) and fluoride around an aluminium smelter in Wales (Richardson 1981). It is also a suitable methodology for surveying for SO2. Lichen samples collected close to industrial complexes emitting SO2 have a much higher sulphur content than samples collected some distance away. Cladonia mitis collected 16km from Copper Cliff nickel smelter, Sudbury, Ontario, Canada had over 1000 µg g-1 dry weight sulphur, more than twice the local background (Nieboer and Richardson 1981). Isotope studies on 34S emitted from natural gas wells in Alberta, Canada showed that the lichens absorbed their sulphur from the air whereas pine needles had sulphur from the soil. This further confirms the advantages of lichens as indicators of air quality (Krouse 1977).

This methodology would seem to have considerable potential in New Zealand. A vast range of "clean" lichens and mosses are available from pollution-free areas like the West Coast of the South Island and it would be relatively cheap to hang such samplers in areas suspected to be polluted. It would be necessary to determine optimal time periods of exposure and preferred sampling species but this would not be difficult. The system is particularly interesting because almost all polluting materials are absorbed and it is, therefore, multipurpose. It would, for instance, be an excellent method for monitoring for agricultural or horticultural spray drift. Analysis of lichens and mosses would provide an exceptionally good method to calculate deposition following rare events like volcanic eruptions but would require that analyses be available of background levels of thallus contents. Surveys of lichens in the vicinity of Mt Etna, Sicily, have been used to track the location of the plume from the volcano by analysing samples for fluoride (Davies and Notcutt 1988). Similar analyses at La

Palma in the Canary Islands have been used to follow the release of toxic gases from lava as it cooled. The lichens revealed that outgassing continued for many years, much longer than previously expected (Davies and Notcutt 1989). A survey of these background levels throughout the country could be a useful preemptive step for detection of rare events.

6.3.2 Marine algae

Because large coastal marine algae (seaweeds) are immersed in seawater and take up substances over the whole of their surface they can also be exceptionally good bioindicators. The brown alga, Fucus vesiculosus, is a well established bioindicator in Europe especially for monitoring radioactive pollution. Concentration factors (Fucus : water) of the order of 103 have been reported. In Ireland the species has been used to track a variety of nuclides originating form the Sellafield reprocessing plant in northern England (Mitchell et al. 1987). It would seem possible that marine algae could be used in New Zealand to track other forms of pollution but considerable calibration work would be needed. With the considerable and growing interest in the maintenance of inshore fish stocks this could yet become an important possibility.

A recent possibility is the use of satellite image analysis with selected spectra to monitor algal (phytoplankton) behaviour in the region of estuaries. This has considerable possibilities for rapid assessment but would also need considerable development (McGarrigle 1987).

6.3.3 Microflora and fauna in freshwater systems

Microfauna and flora in freshwater also provide considerable bioindicator possibilities for similar reasons to marine algae. A large range of organisms can be used from hydroids (Stebbing et al 1983), macrophytes (Whitton 1979), macroinvertebrates and chironomids. Typically some indicator species are used although species composition is also measured. It is important that standard methodologies be used and considerable effort has gone into their development in Europe (Council of the European Communities 1977). Systems are in use in New Zealand but their use is always limited by a need for specialists to make the assessments. Universities are moving to provide specialist training courses for people requiring this expertise.

6.3.4 Leaf Yeasts

Leaf yeasts of the genera Sporobolomyces and Tilletiopsis are easily isolated from the surface of most living leaves into almost pure culture by the spore fall method. Identification can be by colour only and the number of colonies directly reflects the density of sporing cells on the leaves which is affected by air pollutants. In particular SO2 has been found to affect population density so that this methodology can be used to monitor its level (Dowding 1987). Unfortunately the yeast populations also rapidly respond to habitat factors like temperature and moisture so that long-term monitoring is very difficult. It is not likely that the system would be useful in New Zealand.

6.4 Overall summary

1. Bioindicators should provide an excellent, effective and cost-effective method for monitoring air pollution. Useful species are likely to be found in all environments and those used would depend on the environment to be monitored.

2. Bioindication would seem to be particularly useful for air pollution studies where potential polluting sources may not yet be identified or where long-term monitoring is needed. Used in conjunction with suitable calibrating systems it should be possible to get indicative values for air pollution from organisms within the affected habitats.

3. Bioindication relies, to an extent depending on the organisms and methodology used, on specialists skilled in the identification of the organisms. This will normally place constraints on the use of bioindicators in New Zealand unless some simplified sampling procedure can be developed. Constraint will be particularly severe where community structure and species occurrence are used to calculate pollution indices. Constraint is less severe but still present where analyses of elemental composition are used. It is still normally necessary to be able to identify the organism to be analysed but, in this case, a very common or particularly obvious organism can be used.

4. Lichens would seem to be very useful organisms for air pollution studies with both active (change in community structure) and passive (elemental composition) systems being suitable. Transplantation also provides the opportunity to detect local sources of pollution even where lichens may not be present due to lack of suitable substrate. It is unfortunate that the pollutant to which lichens are most sensitive, SO2, is not normally a problem in New Zealand. There is also the problem that the sensitivity of the organisms in relation to those in the Northern Hemisphere (where most studies have been carried out) is not yet known. The limited evidence available would suggest that New Zealand plants could be many times more sensitive than those in long-polluted Europe or North America.

5. a. Passive monitoring involving the analysis of organisms would seem to have the greatest potential in New Zealand. Used correctly it would combine effectiveness with economy.

   b. Lichens or bryophytes would be the best organisms to use since they are proven to be more tightly linked to the air in their elemental composition than trees or other higher plants which source most nutrients from the soil.

   c. Passive monitoring can be applied in two ways both of which would have their uses in New Zealand. First, lichens or bryophytes in situ can be collected and analysed; second, samples of known composition can be placed in the area to be monitored for a selected time and then analysed to determine the change in composition.

d. The first method is an excellent and cost-effective method for monitoring large areas against rare events. Base-line composition data should be collected on a regular basis (multi-annual intervals would probably be satisfactory) and this should be complemented with a secure sample collection that can be analysed later, if required, to enhance information. If such a data set had been in place for the central North Island then the effects of the recent eruptions would have been easily monitored.

e. The second method is highly suitable for concentrated or long-term monitoring of selected areas. In this system bags containing a suitable organism, a bryophyte is usually the best, of known composition is hung in the area and then later analysed. This system has the advantage that it is cheap, little more than the cost of the analyses, unobtrusive and very low-tech, the high-tech part stays in the laboratories. The time period for optimal results would need to be determined by trials. This system is suitable for most pollutants since it does not rely on a reaction by the organism. It would be especially suitable for monitoring drift from horticultural and agricultural spraying. Everything from superphosphate to the most advanced herbicide could be monitored.

7. EFFECTS OF AIR POLLUTION ON BIRDS

Birds have high metabolic rates, and have the potential to be directly affected by ambient air pollution. However, studies have shown that severe effects resulting from gaseous air pollution are rare. The most severe effects on bird populations have been secondary effects, and are largely the result of translocation of the pollutant into an effect in the food chain.

7.1 Acid Pollution

Sulphur Dioxide, nitrogen oxides emissions, in combination with ozone and contributing meteorological conditions, can produce acid deposition into ecosystems. Birds have not displayed any symptoms which would make them early warning indicators of environmental damage from acid pollution, in contrast to lichens or fish, which are much more sensitive. So far there has been little definitive work carried out which identifies a direct effect to birds as a result of acid pollution. There are, however quite a few documentaries of birds suffering secondary effects, via the food chain, as a consequence of acid deposition. These effects can include a reduction to the reproductive success of some bird species, by inducing adverse affects on eggshells quality, clutch size, incubation or hatching success (Llacuna et al, 1995).

Birds suffer from the effects of acid deposition most as a result of loss of food, which may include the loss of calcium in the diet which then affects eggshell strength. This food loss may be a result of acidification of water bodies, which may change the composition and abundance of phytoplankton and zooplankton, which has the dual effect of reducing this food supply to birds, and aquatic invertebrates and fish which rely on this food source, and so the effect is transferred along the food chain (Goriup 1989).

Some insect eating birds (dabbling ducks and grey wagtails) can remain unaffected for some time following increases acidity of the water body, if their competitors for this food, the fish inhabiting the water, have already been adversely affected. But the dipper (*Cinclus cinclus*) suffers badly as it relies heavily on caddisfly larvae and mayfly nymphs during the breeding season, which are severely affected by acidification (Goriup 1989).

Fish populations in standing water bodies are severely threatened by acidification, mostly as a result of the release of ionic aluminium. Smaller fish, in terms of species and age, are the most vulnerable, and the result may be a surviving fish population which is made up only of large fish (Goriup 1989). Experimental studies in Canada have demonstrated that a reduction in pH from 6.8 to 5.0 over a period of eight years caused a number of drastic changes, including the cessation of fish reproduction at pH 5.4 (Roberts, 19??). Another effect is the precipitation of humus, which effectively flocculates the water, resulting in much clearer conditions. This makes hunting for fish easier for birds, but has the net result of adding more stress to the fish populations. (Goriup 1989).

Studies of Loon populations in Ontario have attributed chick mortality directly to malnutrition arising from the lack of adequate nourishment due to the loss of fish populations in nesting territories (Roberts 19??).

Birds which are dependant on the northern hemisphere coniferous forests (which have been most adversely affected by acid pollution) for food and breeding are facing population decline. However, other species, in particular some rare species of woodpecker have benefited from the increase in dead standing timber, which is their preferred habitat. Changes in the forest species population is also benefiting other species such as the black grouse, which prefer the broken tree cover and regeneration scrub species (Goriup 1989).

Passerine birds have larger numbers of erythrocytes and higher concentrations of haemoglobin, compared to other birds and mammals, which is thought to be a physiological adaptation to the high metabolic requirements of flight. During flight, birds increase their metabolic rate much more than mammals, therefore increasing the potential for exposure to air pollution. Llacuna et al (1996), referred to studies which found haematological changes in small mammals after inhaling high levels of SO_2, and in studies on the effects on Passerine birds living in the Cercs area in Spain, showed decreased erythrocyte counts in birds living near a coal fired power station. In this study, the birds were exposed to ambient levels with monthly average SO_2 concentrations ranging from 16 to 974ug/m^3, and monthly average ranges of 0 to 50 ug/m^3 NO_2, . Their results suggested that two species were affected to the degree of displaying a decrease in erythrocyte numbers, and an increase in mean corpuscular volume and mean corpuscular haemoglobin.

An examination carried out by Llacuna et al ,1993, on small birds and wood mice in the Same Cercs area in Spain showed alterations to the tracheal epithelium, an effect which was ascribed to SO_2 and NO_2 emissions from the nearby coal fired power station.

7.2 Heavy Metal Pollution

The major air pollution source of heavy metal contamination is particulate material, mostly origination from combustion sources. Cadmium, mercury and lead can be emitted via air, to become available through soil, water and food. Although normally the amount of cadmium and mercury is inhaled as dust or fumes, the most acute toxicity cases are caused by inhalation (Neathery and Miller, 1975). While the small amounts translocated to plants and the very small degree of absorption by the intestinal tract are two major discriminatory effects against cadmium, lead and mercury entering the food chain of animals; the primary exposure route for birds to heavy metals is from food which has been exposed either directly from fallout, or ingestion.

Comparisons of three passerine bird species living in polluted and non-polluted zones - even where acid precipitation did not necessarily result in the acidification of water bodies - in Northeast Spain demonstrated that levels of Cr, Al were higher for birds living in polluted zones (Llacuna 1995); and that the degree of uptake of specific metals was species specific. Birds which ate only vegetation had lower levels than birds which ate other animals.

Aluminium levels above 0.1% of the diet can have an adverse effect by disrupting Ca and P metabolism. An increased intake of Al by insects inhabiting acidic lake waters, and which are a major food source for pied flycatchers in Sweden, has been linked to severe eggshell defects in flycatcher populations nesting near the affected lake (Scheuhammer, 1987). Measurements of Al concentrations in these insects revealed levels up to 1230ug/g dry weight.

Studies by Nyholm et at,(1995) comparing populations of Passerines in Poland (=polluted environment) and Sweden (=clean environment) showed that ambient levels influenced the body burden for the metals Pb, Cd, Hg which are non-essential elements for the birds physiological development, The essential elements Zn Cu, Fe were not influenced by ambient concentrations, and probably subjected to homeostatic control mechanisms. The same study examined haemoglobin levels in the two populations, and found that levels were lower in birds from the polluted environments, however, whether the cause of lowered haemoglobin is due to heavy metal contamination or gaseous pollutants is not clear.

Cd has been demonstrated to be accumulated by birds in the liver and kidneys in excess of the concentrations in their food supplies; and the organ associated with Cd toxicity is the kidney while the liver, which accumulates approximately half the body burden is generally resistant to Cd toxicity; with the testes of males also affected severely by sub-lethal exposures. Birds accumulating Cd levels of 100-200ug per gram dry weight in the kidneys, have displayed symptoms of Cd induced nephrotoxicity, similar to that found in humans an other mammals (Scheuhammer, 1986).

Severe inhibition of reproductive organs following Hg dietary intake. At levels of 2ppm, delayed testicular development as seen in young quail; levels of 125ppm in drinking water resulted in depressed fertility, and concentrations above 125ppm in drinking water depressed growth rates and increased mortality in young chickens (Scheuhammer, 1986).

Transformation of Hg species in aquatic environments can be complex (Scheuhammer, 1986). The most stable form, MeHg, is the most readily absorbed intestinally, and has been subjected to rigorous study. Species sensitivity to Hg contamination varies, for example, feeding 33ppm Hg (as MeHg) for 35 days to pheasants, ducks chickens resulted in 90%, 85% and 7.5% mortality respectively(Gardiner, 1972 in Scheuhammer, 1986). Piscivorous birds living in a Hg contaminated environment are particularly vulnerable, even if the original source of contamination contained no MeHg. As a result of if its ability to cross the blood-brain barrier birds exposed to this pollutant can suffer spinal cord degeneration. The symptoms of Hg poisoning in birds is similar for many species, and is characterised by reduced food intake which leads to loss of body weight, progressive weakness and difficulty flying or walking and standing, and inability to co-ordinate muscle movements. Death is inevitable. Low doses of 2-3ppm over a period of 12 weeks resulted in liver concentrations of around 2ppm Hg in adults. This affected reproduction, and resulted in an increase in shell-less eggs, decreased hatchability, and an increase in unfertilised eggs.

Lead is absorbed primarily by the bones of birds, and if accumulated in soft tissues, it is mostly by the kidneys. Any excess may be sequestered in the nuclei of cells, where it is bound to nuclear inclusion bodies. Absorption appears to be linked to dietary Ca levels. Female birds will accumulate Pb at a greater rate than males, and this may increase 4-5 times in laying females; which may be related to the greater turnover of skeletal Ca ,which is a result of eggshell formation. This is linked to biochemical processes where increased synthesis of a vitamin D responsive Ca-binding protein appears to be linked to increased intestinal absorption of Pb. Young birds are more susceptible to Pb toxicity, displaying symptoms when crop contents Pb concentration was 80-100ppb, while adult birds from the same nest were unaffected. Growth impairment of nestlings has been associated with kidney levels of around 6ppm, and at 15ppm, survival was at risk. Reproduction does not appear to be affected by dietary levels < 100ppb. Starlings reared with highway verges and exposed to dietary PB levels of around 90ppb displayed decreased brain weights. Some species appear to be more susceptible to Pb toxicity; Japanese quail showed reproductive effects from dietary levels as low as 10ppb, whereas chickens required over 200ppb to produce similar effects (Scheuhammer, 1986)..

7.3 Spray Drift

Spray drift impacts on no-target species has the potential to impact on ecosystems, particularly if the exposure is a significant one, and herbicide spray drift can have severe economic effects.

Pesticide spray drift was shown to have an impact on aquatic organisms to 120m from application source by Helson et al, 1993. Selectively reducing the pesticide inputs into the headlands of cereal fields on a farm in Hampshire (a technique known as "conservation headlands" resulted in increased numbers of butterflies (Dover et al, 1990). In a study using *Pieris rapae* larvae as bioassays of deltamethrin toxicity, Cilgi and Jepson, 1994, modelled spray drift exposure levels and predicted mortalities with distance away from the source, with the recommendation that conservation headland management techniques be utilised in Great Britain to protect non-target species.

The inhabitants of extensive hedgerows of Europe and Great Britain, including birds and insects, have been the subject of studies on the impacts of spray drift (Cordi et al, 1997). Hedgerows, copses and spinneys have become increasingly important conservation area, providing connecting corridors to facilitate the movements of many mammals and birds. Cordi et al, 1997, found that wild Prasserine nestlings were affected by pirimicarb and dimethoate spray exposures. While older chicks showed delayed development and reduced weight, young chicks did not possess sufficient body mass to process the chemicals, and did not survive the exposures.

8. AMBIENT AIR QUALITY GUIDELINES

The evaluation of the potential impacts from air pollution on ecosystems, brings together evaluations of physiological responses to elements which can cause imbalances of one kind or another, and the conditions under which the exposure occurs, and whether this combination will create a severe effect. An extremely important factor to consider here is climatic influence, as this influences both the pollutant concentrations, and the degree of gas exchange between the plant and the surrounding atmosphere. In the case of exposures to NOx and SO2, plants are most susceptible during colder months of the year than the warm, summer months, due to decreased stomatal resistance during winter, which also coincides with higher air pollution levels. It is important to retain this in the evaluation of potential damage to New Zealand plants, which have relatively fast growth rates, and are growing in a much milder climate with longer photoperiods and higher light intensities (refer Dodd and Doley, 1988).

While nitrogen and sulphur oxides are capable of producing severe acute affects at high concentrations, and also chronic, and possibly long-term effects at low levels, the most serious effects that air pollution has had on forests and ecosystems generally, has resulted from interactions where the pollution has “tipped the scales” in pre-existing vulnerable situations. As the preceding discussions have indicated, where severe effects on systems from air pollution have occurred as a result of acid deposition, the “weakness” in the systems was ineffectual buffering capacity in the soil.

Ozone and fluoride differ, in being extremely phytotoxic at very low levels, and therefor possess the potential to produce severe effects regardless of other imbalances.

But nevertheless, meteorological influences are an important consideration also, both in influencing the ambient air concentrations and a plant’s physiological processes. In summary, when taking all matters discussed into consideration, if individual point sources of SO_2 and NO_2, and also fluoride, attained high enough levels, they may have an impact on local ecosystems. It is a different scenario for ozone, because the generation of ozone is dependant on warm temperatures and high light intensity as well as concentrations of the precursor elements, and is most likely to be “exported” from the original pollutant source region. In New Zealand, the potential ozone impact areas have been identified as areas surrounding the cities of Auckland, Hamilton and Christchurch.

8.1 Oxides of Nitrogen

.The New Zealand Ministry for the Environment has set ambient air guidelines for nitrogen dioxide only, for the reason that it has human health effects.

The effects of oxides of nitrogen on plants is confounded by many factors;

- nitrogen is an essential element for plants, and the effect resulting from exposure to oxides of nitrogen will be dependant on whether the existing nitrogen supply is limiting or adequate (Bytnerowicz and Grulke)

- nitrogen dioxide may enter leaves through the cuticle as well as through the stomata
- night time exposures are more likely to cause damage due to the lack of nitrate reductase activity which enables the plant to undertake detoxifying metabolic processes
- all ambient nitrogen has the potential to impact on plants

Table 4 Ministry for the Environment Ambient Air Guidelines - Nitrogen Dioxide

	1 hour	24 hour
Nitrogen Dioxide	$300\mu g/m_3$	$100\mu g/m_3$

It is likely that the guideline level for nitrogen dioxide is adequate as a single pollutant. However, consideration should also be given to the effects that other nitrogen species, such as ammonia and nitric oxide, may have on plants on plants.

8.2 Sulphur Dioxide

Reduction in yield have been recorded for perennial ryegrass at $43\mu g/m_3$ SO_2 exposure for 273 days, and in tobacco and cucumber at $55\mu g/m_3$ following 28 days exposure. Foliar injury has been reported from “long term” exposures at 20 - $40\mu g/m_3$ in *Picea* and *Betula* spp.

These results indicate that the present Ministry for the Environment guidelines for sulphur dioxide will not protect sensitive species.

More work would be required to establish if similar results occurred under the New Zealand growing conditions.

Table 5 Ministry for the Environment Ambient Air Guidelines - Sulphur Dioxide

	10 min	1 hour	24 hour	Annual
Sulphur Dioxide	$500\mu g/m_3$	$350\mu g/m_3$	$125\mu g/m_3$	$50\mu g/m_3$

8.3 Fluoride

The Ministry for the Environment's Guidelines for fluoride include all those recommended by ANZECC. The intention was to follow these guidelines until data on New Zealand native species and their vulnerability has been gathered and analysed for purposes of setting an ambient guideline.

Table 6 Ministry for the Environment Ambient Air Guidelines - Fluoride, Special Land Use

Special Land Use	12 hour	24 hour	7 day	30 day	90 day
Fluoride	1.8µg/m_3	1.5µg/m_3	0.8µg/m_3	0.4µg/m_3	0.25µg/m_3

Table 7 Ministry for the Environment Ambient Air Guidelines - Fluoride, General Land Use

General Land Use	12 hour	24 hour	7 day	30 day	90 day
Fluoride	3.7µg/m_3	2.9µg/m_3	1.7µg/m_3	0.84µg/m_3	05µg/m_3

At this stage there is no evidence to suggest that these guidelines need to be changed.

8.4 Ozone

It is very difficult to set guidelines for ozone since there is a strong interaction between level and time of exposure.

The New Zealand Ministry for the Environment guideline levels for humans are 150 µg m^{-3} over a one hour average and 100 µg m^{-3} over an 8-hour period (Anon. 1994). For plants, threshold concentrations that have shown an effect are 200 µg m^{-3} over 1 hour, 65 µg m^{-3} over 24 hours and 60 µg m^{-3} over 100 days growing season (Jacobson 1977). Both subtle and chronic effects of ozone fail to appear if levels remain below 60 µg m^{-3} (7 hour per day average).

Adverse pollen production, pollen distribution, pollen germination, seed production, germination and flower initiation effects have all been reported as consequences of ozone exposure.

Table 8 Ministry for the Environment Ambient Air Guidelines - Ozone

	1 hour	8 hour
Ozone	150µg/m_3	100µg/m_3

8.5 Particulate

There are no adequate investigations on the effects particulate deposition may have on plants.

Studies on the results of various animal exposures to particulate material have not tried to relate measurements to particulate deposition. In addition, the uptake routes and variety of exposure mechanisms of animals to particulate deposition, and the lack of identification of the pollutant as a proportion of particulate, mean that it is not possible to relate many of the measured effects to actual deposition rates of the pollutant.

8.6 Synergistic and Additive Effects

The fact that ground level ozone pollution is on the rise at the same time as less sulphur (from reduced sulphur emissions) to help plants combat the effects of ozone, raises the question of just what should be acceptable guidelines for air pollution levels for 0_3, $S0_2$ etc. In 1985, European countries pledged to reduce their sulphur emissions by at least 30% by 1993 and most have done so (MacKenzie 1995). The sulphur deposited on European fields has fallen from ~50 kg/ha in the 1970s to ~10 kg/ha now. It is not clear though whether published air quality guidelines, either in Europe or in New Zealand, make allowance for either i) the minimum plant requirements (at low levels) or ii) the capacity for seed/reproductive damage (at high levels).

The major concern has usually been the contribution of $S0_2$ to acid rain, human and animal responses. The New Zealand Ministry for the Environment Ambient Air Quality guidelines (1994), for example, make little mention of any plant effects. Acceptable levels of 500 µg/m^3 (10 minutes); 350 µg/m^3 (1 hour); 125 µg/m^3 (24 hours); 50 µg/m^3 (year) are purely human health based guidelines. USEPA guidelines are set at 80 µg/m^3 (annual) and 365 µg/m^3 (1 hour); WHO air quality guidelines for Europe set the much lower levels of 10-30 µg/m^3 (year) as being critical for ecotoxic (vegetation) effects (especially alfalfa, barley, red clover, oat, aster, aspen, birch and jack pine) (Krupa 1996). In contrast, pinus and oak species seem relatively resistant (WHO, 1987). The New Zealand guideline level set for ozone is 150 µg/m^3 (for 1 hour) or 100 µg/m^3 (for 8 hours), compared to naturally-occurring background levels of 0-65 µg/m^3. (NB these guidelines are significantly less stringent than the informal Department of Health guidelines of 120-60 µg/m^3, respectively, though broadly comparable to WHO guidelines for Europe of 0.5-10 ppm h (for 5 days - 6 months) and more stringent than USEPA National Ambient Air Quality Standards (NAAQS) of 235 - 157 µg/m^3).

The MfE guidelines mention 100 µg/m^3 of ozone as causing crop loss (in the US). *Nicotiana tabacum* damage has, however, been reported at as little as 55-80 µg/m^{-3} in the UK (a concentration which can occasionally be reached by natural sources of ozone alone (Ashmore et al 1980; Mejstrik 1980)). Highest levels occur in summer, with high sunshine levels, (though plants are often more sensitive to $S0_2$ stress in winter) (Bell and Clough 1973). Levels of atmospheric ozone have also more than doubled in the past 100 years (Anon. 1994). New Zealand background levels could be expected to exceed those of the UK, in which case levels of 100 µg/m^3 could be easily reached and exceeded, with only a small additional pollutant input. Most reported damage to seed production, however, occurs at the somewhat higher rates of 140 µg/m-^{3}, or higher (Ormrod 1996). (NB: while 200 µg/m^3 might cause damage within 1 hour, only 65 µg/m^3 might be needed at 24 hours, or only 60 µg/m^3 over 100 days (one growing season) (WHO, 1987).

Some commonly encountered levels (1 hour averages) of $S0_2$ and 0_3, reviewed in (Krupa 1996) range from ≤0.05 ppm 0_3 and ≤1 ppb $S0_2$ (“remote”); 0.02-0.08 ppm 0_3 + 1-30 ppb $S0_2$ (“rural”); 0.1-0.2 ppm 0_3 + 0.03-0.2 ppm $S0_2$ (“moderately polluted”); to 0.2-0.5 ppm 0_3 + 0.2-2 ppm $S0_2$ (“heavily polluted”). This would put the New Zealand MfE guideline levels of 350 µg/m^{-3} $S0_2$ (0.175 ppm) + 150 µg/m^{-3} 0_3 (0.075 ppm) into the “moderately polluted” and “rural” categories, respectively.

One problem here is that plants respond to cumulative ozone doses (Nouchi and Aoki 1979). Conventional “threshold” guidelines may not always, therefore, be very useful. As a result, there have been some recent attempts to improve on this approach using a specially-developed model to calculate specific exposure-response functions, related to plant activity (Finnan et al 1997). These have, in turn, been used to reassess much previously-published work concerning ozone effects on plants (Heck et al 1983; Unsworth and Geissler 1993; Fuhrer 1993; Hogsett et al 1988).

Based on these arguments, and the potential for a wide range of effects, as careful review of the way in which O_3 is regulated, with respect to plant injury, is required.

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